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(54) Title: LAUNDRY DETERGENTS COMPRISING MODIFIED AND ENHANCED ALKYLBENZENE SULFONATES

(57) Abstract: Surfactant mixtures, improved detergent and cleaning products containing particular types of alkylbenzene sulfonate surfactants.

LAUNDRY DETERGENTS COMPRISING MODIFIED AND ENHANCED ALKYLBENZENE
SULFONATES

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FIELD OF THE INVENTION

The present invention relates to particular types of alkylbenzene sulfonate surfactant mixtures adapted for laundry and cleaning product use by controlling compositional parameters, especially a 2/3-phenyl index, a 2-methyl-2-phenyl index and linearity, as well as to improved detergent and cleaning products containing these surfactant mixtures, to alkylbenzene precursors for the surfactant mixtures, and to methods of making the precursors as well as the surfactant mixtures. The present compositions are especially useful for fabric laundering.

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BACKGROUND OF THE INVENTION

Historically, highly branched alkylbenzene sulfonate surfactants, such as those based on tetrapropylene, known as "ABS" or "TPBS", were used in detergents. However, these were found to be very poorly biodegradable. A long period followed of improving manufacturing processes for alkylbenzene sulfonates, making them as linear as practically possible, hence the acronym "LAS". The overwhelming part of a large art of linear alkylbenzene sulfonate surfactant manufacture is directed to this objective. However, linear alkylbenzene sulfonates are not without limitations; for example, they would be more desirable if improved for hard water cleaning and/or cold water cleaning properties. They can often fail to produce good cleaning results, for example when formulated with nonphosphate builders and/or when used in hard water areas.

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As a result of the limitations of the alkylbenzene sulfonates, consumer cleaning formulations have often needed to include a higher level of co-surfactants, builders, and other additives than would have been needed given a superior alkylbenzene sulfonate. Yet another currently unresolved problem in alkylbenzene sulfonate manufacture is to make more effective use of current LAB feedstock. It would be highly desirable, both from a performance point of view and from an economic point of view, to better utilize certain desirable types of branched hydrocarbons.

Accordingly there exists a substantial unmet need for further improvements in alkylbenzene sulfonate surfactant mixtures. Improved alkylbenzene sulfonates should provide one or more of the following advantages: superior cleaning, hardness tolerance, biodegradability and cost.

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SUMMARY OF THE INVENTION

It has now surprisingly been found that there exist certain alkylbenzene sulfonate surfactant mixtures, hereinafter "enhanced alkylbenzene sulfonate surfactant mixtures" which offer one or more, and even several of the above-outlined advantages. The discovery of these 10 mixtures solves important problems of the kind described in the background.

More specifically, it has now surprisingly been found for that the alkylbenzene sulfonate surfactant mixtures of the present invention provide superior cleaning performance, cost advantage, along with good biodegradability as compared to conventional alkylbenzene sulfonate surfactant mixtures. In most cases, standard environmental tests, such as the previously described 15 Modified SCAS, are sufficient in determining acceptable surfactant biodegradability. It has additionally been discovered that the alkylbenzene sulfonate surfactant mixtures of the present invention afford a further improved performance and biodegradation profile over the prior art. The present invention achieves the further improved profile by optimizing key compositional parameters, including, but not limited to, the 2/3-phenyl index, the 2-methyl-2-phenyl index and 20 overall linearity. These features provide superior cleaning performance to those who practice the invention, while providing globally acceptable protection of the environment during and following such practice.

In a first aspect of the present invention, an enhanced alkylbenzene sulfonate surfactant mixture is provided.

25 In a second aspect of the present invention, a process for making an alkylbenzene sulfonate surfactant mixture, and an alkylbenzene sulfonate surfactant mixture made by such process is provided.

In still another aspect of the present invention, detergent compositions, especially laundry detergent compositions, comprising the enhanced alkylbenzene sulfonate surfactant mixture of the 30 present invention are provided.

The present invention, on the other hand, is not intended to encompass any wholly conventional alkylbenzene sulfonate compositions or the derivative detergent compositions, such as those based exclusively on linear alkylbenzene sulfonates made by any process, or exclusively on known unacceptably branched alkylbenzene sulfonates such as ABS or TPBS.

In yet another aspect of the present invention, an enhanced alkylbenzene mixture is provided.

In accordance with other embodiments of the present invention, there are encompassed herein a number of alternate and less preferred embodiments, such as those in which there is blending of the enhanced alkylbenzene sulfonate surfactant mixture of the invention with one or 5 more other alkylbenzene sulfonate surfactants. In practical terms, such blending is usually encompassed before sulfonation and detergent formulation, but the outcome is a surfactant mixture or detergent composition containing a blend of the enhanced alkylbenzene sulfonate surfactant with other, known, alkylbenzene sulfonates. Such alternate embodiments of the invention nonlimitingly include those termed herein as "medium 2/3-phenyl surfactant mixtures".

10 Preferred cleaning composition embodiments also contain specific cleaning adjuncts defined hereafter. Moreover, the invention encompasses less preferred but sometimes useful embodiments for their normal purposes, such as the addition of useful hydrotrope precursors and/or hydrotropes, such as C₁-C₈ alkylbenzenes, more typically toluenes, cumenes, xylenes, naphthalenes, or the sulfonated derivatives of any such materials, minor amounts of any other 15 materials, such as tribranched alkylbenzene sulfonate surfactants, dialkylbenzenes and their derivatives, dialkyl tetralins, wetting agents, processing aids, and the like. It will be understood that, with the exception of hydrotropes, it will not be usual practice in the present invention to include any such materials. Likewise it will be understood that such materials, if and when they interfere with analytical methods, will not be included in samples of compositions used for 20 analytical purposes.

The abovementioned embodiments and other aspects of the present invention are more fully described and exemplified in the detailed description hereinafter.

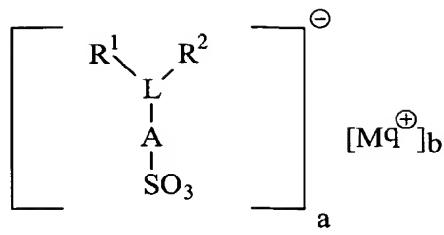
25 All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

First Embodiment:

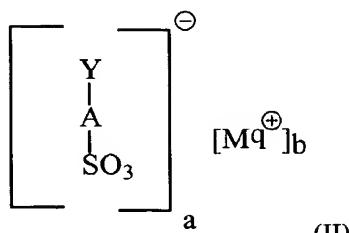
A. Enhanced Alkylbenzene Sulfonate Surfactant Mixtures

30 The present invention encompasses an enhanced alkylbenzene sulfonate surfactant mixture comprising (preferably, consisting essentially of): (a) from about 60% to about 25% by weight, preferably from about 55% to about 35%, more preferably from about 50% to about 40% of a mixture of enhanced alkylbenzene sulfonates having formula (I):



(I)

wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen, said L having two methyl termini and said L having no substituents other than A, R¹ and R²; and wherein said mixture of enhanced alkylbenzene sulfonates contains two or more (preferably at least three, optionally more) of said enhanced alkylbenzene sulfonates differing in molecular weight of the anion of said formula (I) and wherein said mixture of enhanced alkylbenzene sulfonates has a sum of carbon atoms in R¹, L and R² of from 9 to 15 (preferably from 10 to 14); an average aliphatic carbon content (i.e., based on R¹, L and R² and excluding A) of from about 10.0 to about 14.0 carbon atoms (preferably from about 10.5 to about 12.5, more preferably from about 11.0 to about 12.0); M is a cation or cation mixture (preferably selected from H, Na, K, Ca, Mg and mixtures thereof, more preferably selected from H, Na, K and mixtures thereof, more preferably still, selected from H, Na, and mixtures thereof) having a valence q (typically from 1 to 2, preferably 1); a and b are integers selected such that said enhanced alkylbenzene sulfonates are electroneutral (a is typically from 1 to 2, preferably 1, b is 1); R¹ is C₁-C₃ alkyl (preferably C₁-C₂ alkyl, more preferably methyl); R² is selected from H and C₁-C₃ alkyl (preferably H and C₁-C₂ alkyl, more preferably H and methyl, more preferably H and methyl provided that in at least about 0.5, more preferably 0.7, more preferably 0.9 to 1.0 mole fraction of said enhanced alkylbenzene sulfonates, R² is H); A is a benzene moiety (typically A is the moiety -C₆H₄-, with the SO₃ moiety of Formula (I) in *para*- position to the L moiety, though in some proportion, usually no more than about 5%, preferably from 0 to 5% by weight, the SO₃ moiety is *ortho*- to L); and (b) from about 40% to about 75% by weight, preferably from about 45% to about 65%, more preferably from about 50% to about 60% of a mixture of modified unsubstituted alkylbenzene sulfonates having formula (II):



(II)

wherein a, b, M, A and q are as defined hereinbefore and Y is a linear aliphatic moiety having no substituents other than A consisting of carbon and hydrogen having two methyl termini, and wherein said Y has a sum of carbon atoms of from 9 to 15, preferably from 10 to 14, and said Y has an average aliphatic carbon content of from about 10.0 to about 14.0 (preferably from about 5 10.5 to about 12.5, more preferably 11.0 to about 12.0 carbon atoms); and wherein said modified unsubstituted alkylbenzene sulfonate is further characterized by a 2/3-phenyl index of from about 275 to about 10,000, preferably from about 300 to about 5,000, more preferably from about 325 to about 2,500.

A preferred modified unsubstituted alkylbenzene sulfonate has M selected from H, Na, K 10 and mixtures thereof, said a=1, said b=1, said q=1, and said enhanced alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than about 0.3, preferably less than about 0.2, more preferably from 0 to about 0.1.

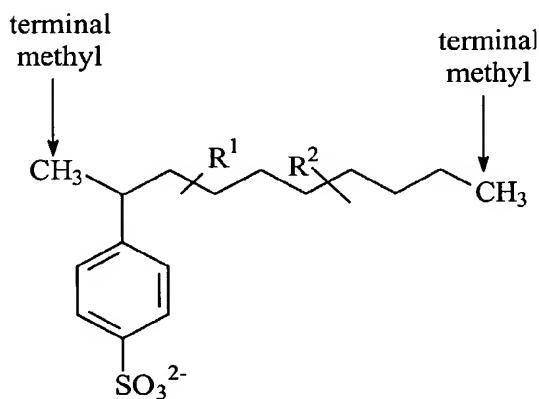
Such an enhanced alkylbenzene sulfonate surfactant mixture according to the first embodiment can be made as the product of a process using as alkylation catalyst a zeolite selected 15 from mordenite, offretite and H-ZSM-12 in at least partially acidic form, preferably an acidic mordenite. Moreover, any alkylation catalyst that exhibits the same or similar characteristics as those of mordenite, under the same or similar conditions, may be employed in the process of making the enhanced alkylbenzene surfactant mixture according to the first embodiment. For instance, certain forms of zeolite beta that exhibit the same or similar characteristics as those of 20 mordenite under the same or similar conditions may be employed as an alternative to mordenite, but are not highly preferred. Embodiments described in terms of their making, as well as suitable catalysts, are all further detailed hereinafter.

Another preferred enhanced alkylbenzene sulfonate surfactant mixture according to the first embodiment of the invention consists essentially of said mixture of enhanced alkylbenzene sulfonates and modified unsubstituted alkylbenzene sulfonates, wherein said 2-methyl-2-phenyl index of said enhanced alkylbenzene sulfonate surfactant mixture is less than about 0.1, and wherein in said mixture of enhanced and modified unsubstituted alkylbenzene sulfonates, said 25 average aliphatic carbon content is from about 11.0 to about 12.0 carbon atoms; said R¹ is methyl; said R² is selected from H and methyl provided that in at least about 0.7 mole fraction of said enhanced alkylbenzene sulfonates R² is H; and wherein said sum of carbon atoms in R¹, L and R² 30 is from 10 to 14; and further wherein in said mixture of modified unsubstituted alkylbenzene sulfonates, said Y has a sum of carbon atoms of from 10 to 14 carbon atoms, said average aliphatic carbon content of said modified unsubstituted alkylbenzene sulfonates is from about

11.0 to about 12.0 carbon atoms, and said M is a monovalent cation or cation mixture selected from H, Na and mixtures thereof.

Definitions:

5 Methyl termini The terms "methyl termini" and/or "terminal methyl" mean the carbon atoms that are the terminal carbon atoms in alkyl moieties, that is L, and/or Y of formula (I) and formula (II) respectively are always bonded to three hydrogen atoms. That is, they will form a CH₃- group. To better explain this, the structure below shows the two terminal methyl groups in an alkylbenzene sulfonate.



10 The term "AB" herein when used without further qualification is an abbreviation for "alkylbenzene" of the so-called "hard" or nonbiodegradable type, which on sulfonation forms "ABS". The term "LAB" herein is an abbreviation for "linear alkylbenzene" of the current commercial, more biodegradable type, which on sulfonation forms linear alkylbenzene sulfonate, or "LAS". The term "MLAS" herein is an abbreviation for the enhanced alkylbenzene sulfonate surfactant mixtures of the invention.

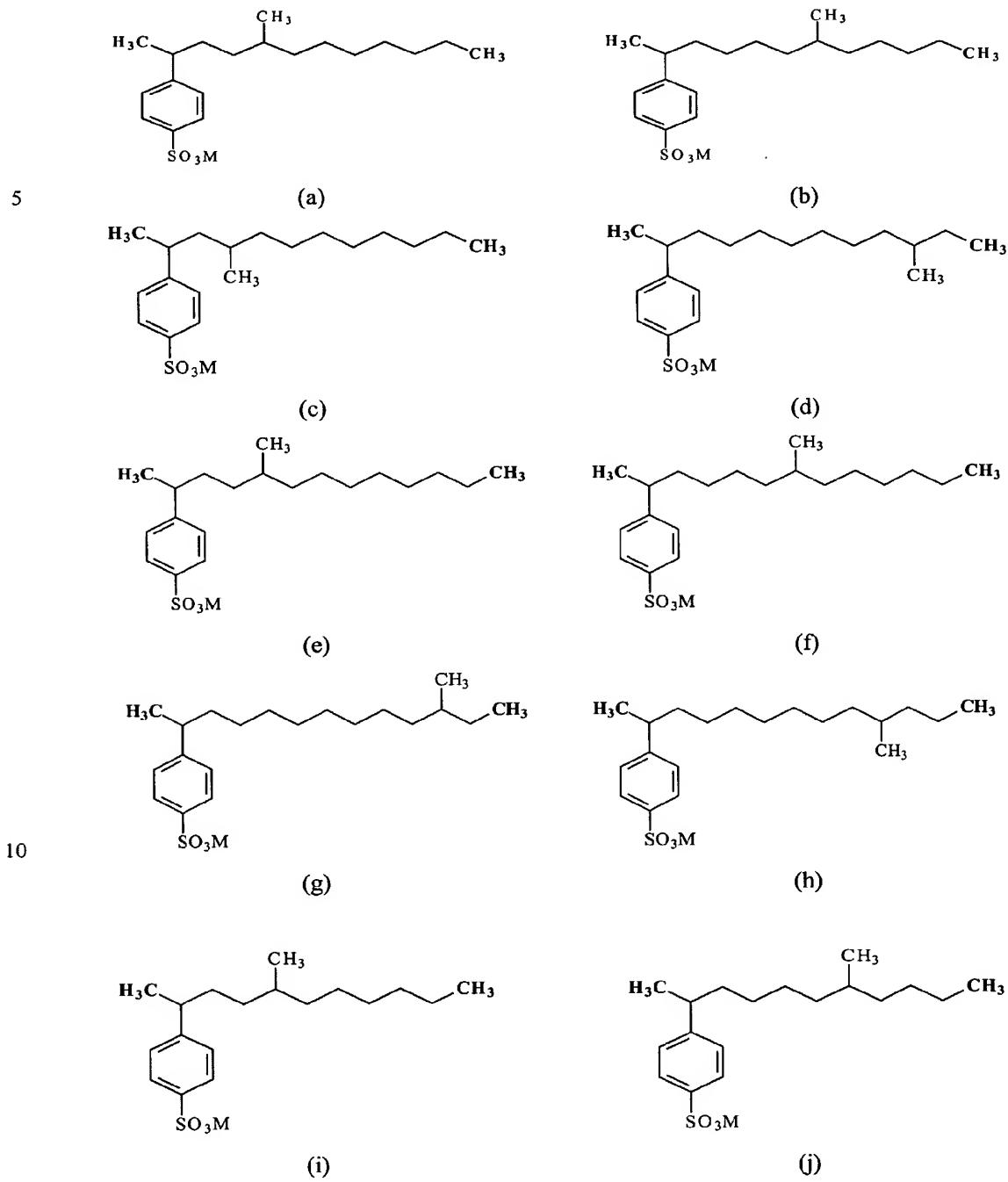
15 Impurities: The enhanced alkylbenzene sulfonate surfactant mixtures herein are preferably substantially free from impurities selected from tribranched impurities, dialkyl tetralin impurities and mixtures thereof. By "substantially free" it is meant that the amounts of such impurities are insufficient to contribute positively or negatively to the cleaning effectiveness of the composition.

20 Typically there is less than about 5%, preferably less than about 1%, more preferably about 0.1% or less of the impurity, that is typically no one of the impurities with practical analytical detection limits.

Illustrative Structures

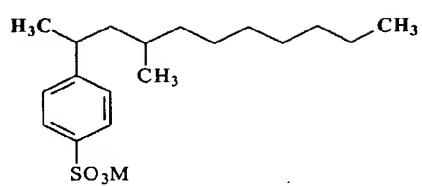
25 The better to illustrate the possible complexity of the enhanced alkylbenzene sulfonate surfactant mixtures of the invention and the resulting detergent compositions, structures (a) to (v)

below are illustrative of some of the many preferred compounds of formula (I). These are only a few of hundreds of possible preferred structures that make up the bulk of the composition, and should not be taken as limiting of the invention.

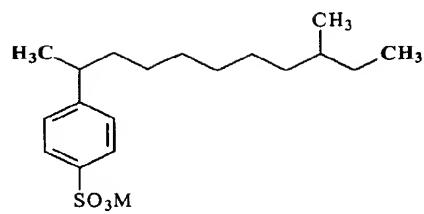


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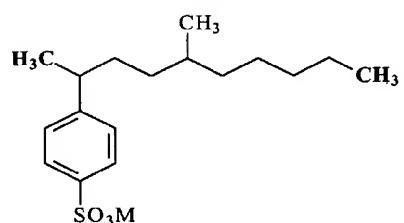
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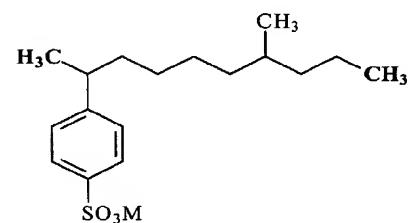
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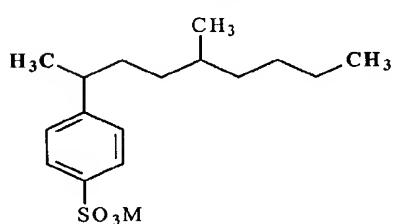
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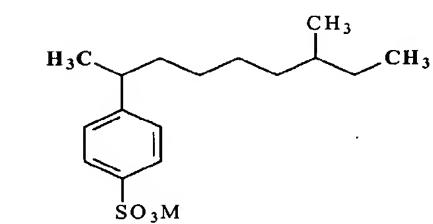
(m)



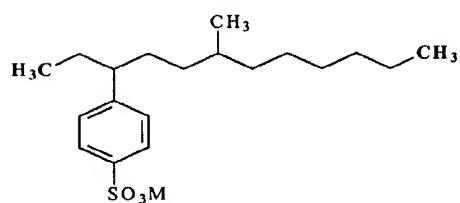
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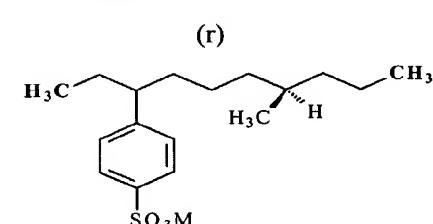
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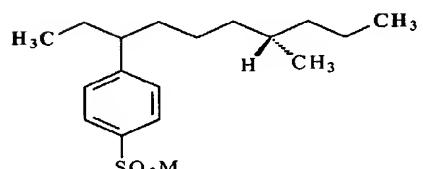
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(q)

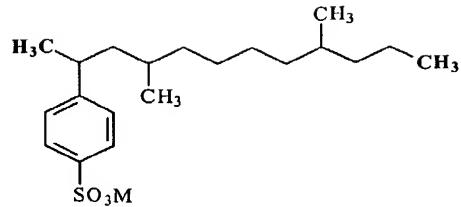


(r)

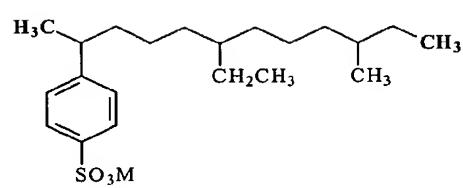


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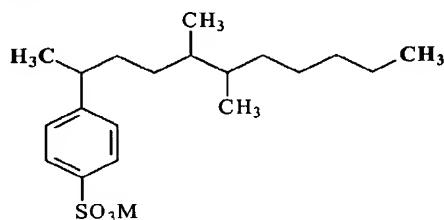


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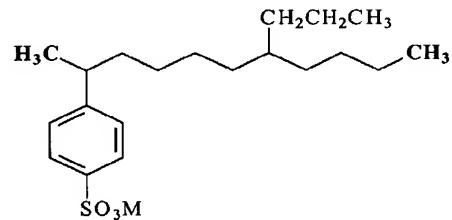


(v)

5 Structures (w) and (x) nonlimitingly illustrate less preferred compounds of Formula (I) which can be present, at lower levels than the above-illustrated preferred types of structures, in the enhanced alkylbenzene sulfonate surfactant mixtures of the invention and the resulting detergent compositions.

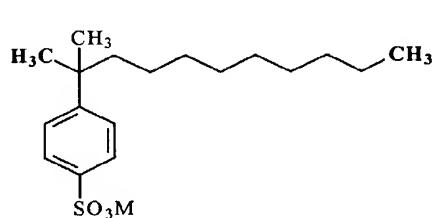


(w)

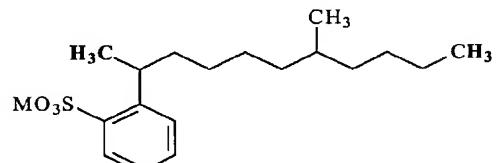


(x)

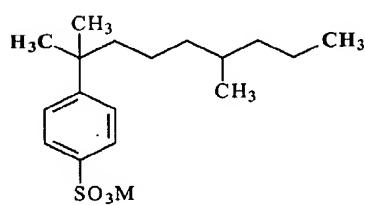
10 Structures (y), (z), and (aa) nonlimitingly illustrate compounds broadly within Formula (I) that are not preferred but which can be present in the enhanced alkylbenzene sulfonate surfactant mixtures of the invention and the resulting detergent compositions.



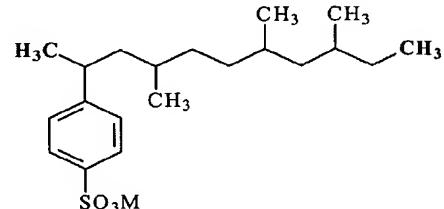
(y)



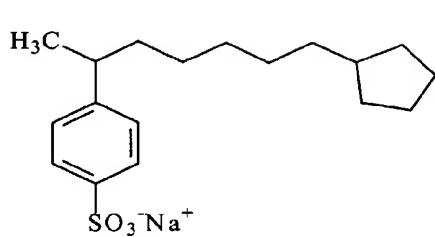
(z)



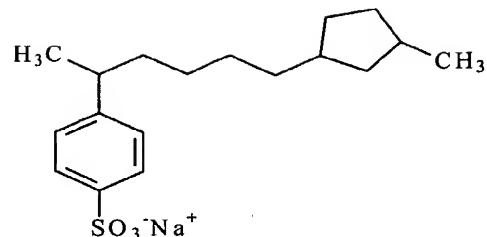
(aa)



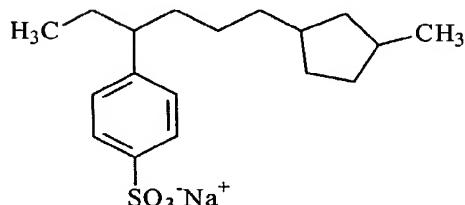
(bb)



(cc)



(dd)



(ee)

Structure (bb) is illustrative of a tri-branched structure not within Formula (I), but that can be present as an impurity.

Structures (cc), (dd) and (ee) are illustrative of structures not within Formula (I), but that can be present as impurities.

10 **First Embodiment:**

B. Enhanced alkylbenzene sulfonate surfactant mixtures defined on the basis of their preparation

Preferably the enhanced alkylbenzene sulfonate surfactant mixtures herein are the product of sulfonating the corresponding enhanced alkylbenzene mixtures, wherein the enhanced alkylbenzene is produced by alkylating benzene with a substituted olefin, and more particularly the lightly substituted types described in more detail hereinafter, over an acidic mordenite-type catalyst, or other suitable catalyst as defined elsewhere herein.

In outline, enhanced alkylbenzene sulfonate surfactant mixtures herein can be made by the steps of:

20 (I) alkylating benzene with an alkylating mixture;
 (II) sulfonating the product of (I); and (optionally but very preferably)
 (III) neutralizing the product of (II).

Provided that suitable alkylation catalysts and process conditions as taught herein are used, the product of step (I) is an enhanced alkylbenzene mixture in accordance with the invention. Provided that sulfonation is conducted under conditions generally known and reapplicable from LAS manufacture, see for example the literature references cited herein, the

product of step (II) is an enhanced alkylbenzene sulfonic acid mixture in accordance with the invention. Provided that neutralization step (III) is conducted as generally taught herein, the product of step (III) is an enhanced alkylbenzene sulfonate surfactant mixture in accordance with the invention. Since neutralization can be incomplete, mixtures of the acid and neutralized forms 5 of the present enhanced alkylbenzene sulfonate surfactant mixtures in all proportions, e.g., from about 1000:1 to 1:1000 by weight are also part of the present invention. Preferably, said alkylating mixture contains said branched C₉-C₂₀ monoolefins having at least two different carbon numbers in said C₉-C₂₀ range, and has a mean carbon content of from about 9.0 to about 15.0 carbon atoms; and wherein said components (a) and (b) are at a weight ratio of at least about 10 15:85.

Preferred enhanced alkylbenzene sulfonate surfactant mixtures herein comprise the product of a process comprising the steps of: (I) alkylating benzene with an alkylating mixture; (II) sulfonating the product of (I); and (optionally but very preferably) (III) neutralizing the product of (II); wherein said alkylating mixture comprises: (a) from about 1% to about 99.9%, by 15 weight of methyl-substituted C₉-C₁₅ (preferably C₁₀-C₁₄) monoolefins, said substituted monoolefins having structures identical with those of the substituted monoolefins formed by dehydrogenating substituted paraffins of formula R¹LR² wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen and containing two terminal methyls; R¹ is C₁ to C₃ alkyl; and R² is selected from H and C₁ to C₃ alkyl; and (b) from about 0.1% to about 85%, by weight of C₉- 20 C₁₅ (preferably C₁₀-C₁₄) linear aliphatic olefins; wherein said alkylating mixture contains said methyl-substituted C₉-C₁₅ monoolefins having at least two different carbon numbers in said C₉-C₁₅ range, and has a mean carbon content of from about 9.0 to about 15.0 carbon atoms (preferably from about 10.0 to about 14.0, more preferably from about 10.5 to about 12.5, more preferably still from about 11.0 to about 12.0); and wherein said components (a) and (b) are at a weight ratio of at least about 15:85 (preferably having methyl-substituted component (a) & modified unsubstituted component (b) in a performance and biodegradation optimum ratio, for example from 25% to 60% of (a) and 40% to 75% of (b), more preferably 35% to 55% of (a) and 45% to 65% of (b), more preferably still 40% to 50% of (a) and 50% to 60% of (b), wherein these percentages by weight exclude any other materials, for example diluent hydrocarbons, that may be present in the process). Said monoolefins (a) or (b) may be internal monoolefins, alpha-olefins, and/or mixtures thereof. They may be diluted with certain materials selected from paraffins and inert, non-paraffinic solvents. Further, the resultant olefin/paraffin mixture may be obtained via the dehydrogenation of a paraffin mixture obtained from kerosene feed stock via a molecular sieving unit designed to isolate a mixture, consisting mainly of both linear and

monomethyl branched paraffins from cyclic and dimethyl branched paraffins. Said mixture is blended, if needed, to achieve a linear content of 40% to 75%.

In yet another preferred embodiment, the invention encompasses an enhanced alkylbenzene sulfonate surfactant mixture prepared in accordance with the above-outlined steps 5 wherein said alkylating mixture may be obtained via any one of the following:

- 1) Dimerization of short chain olefin mixtures inside a molecular sieve
- 2) Oligomerization of short chain olefin mixtures inside a molecular sieve
- 3) Product of cracking long-chain hydrocarbon waxes under conditions to obtain a mainly mono methyl branched olefin product;
- 10 4) Dehydrogenation of a paraffin mixture obtained from a gas to liquids (GTL) plant.

Other enhanced alkylbenzene sulfonate surfactant mixtures herein are made by the above-outlined processes wherein in step (I), said alkylation is performed in the presence of an alkylation catalyst, said alkylation catalyst is an intermediate acidity solid porous alkylation catalyst, and step (II) comprises removal of components other than monoalkylbenzene prior to 15 contacting the product of step (I) with sulfonating agent.

Also encompassed is the enhanced alkylbenzene sulfonate surfactant mixture according to the above-defined processes wherein said alkylation catalyst is other than a member selected from the group consisting of HF, AlCl₃, sulfuric acid and mixtures thereof. Such is the case when the alkylation catalyst is selected from the group consisting of non-fluoridated acidic mordenite-type 20 catalyst, fluoridated acidic mordenite-type catalyst and mixtures thereof.

The processes are tolerant of variation, for example conventional steps can be added before, in parallel with, or after the outlined steps (I), (II) and (III). This is especially the case for accommodating the use of hydrotropes or their precursors. Thus the invention encompasses an enhanced alkylbenzene sulfonate surfactant mixture according to the above-outlined processes 25 wherein a hydrotrope, hydrotrope precursor, or mixtures thereof is added after step (I); or the hydrotrope, hydrotrope precursor or mixtures thereof is added during or after step (II) and prior to step (III); or a hydrotrope can be added during or after step (III).

In certain cases, compositions herein can also be prepared by blending. Thus, the invention includes a detergent composition using an enhanced alkylbenzene sulfonate surfactant 30 blend according to the first embodiment wherein said enhanced alkylbenzene sulfonate surfactant mixture is prepared by a process comprising a step selected from: (i) blending a mixture of enhanced and modified unsubstituted alkylbenzene sulfonate surfactants having a 2/3-phenyl index of 500 to 700 with an alkylbenzene sulfonate surfactant mixture having a 2/3-phenyl index of 75 to 160 and (ii) blending a mixture of methyl-substituted and modified unsubstituted

alkylbenzenes having a 2/3-phenyl index of 500 to 700 with an alkylbenzene mixture having a 2/3-phenyl index of 75 to 160 and sulfonating said blend.

Sulfonation and Workup or Neutralization (Steps II / III)

In general, sulfonation of the enhanced alkylbenzene mixture in the instant process can 5 be accomplished using any of the well-known sulfonation systems, including those described in "Detergent Manufacture Including Zeolite Builders and other New Materials", Ed. Sittig., Noyes Data Corp., 1979, as well as in Vol. 56 in "Surfactant Science" series, Marcel Dekker, New York, 1996, including in particular Chapter 2 entitled "Alkylarylsulfonates: History, Manufacture, Analysis and Environmental Properties", pages 39-108 which includes 297 10 literature references. This work provides access to a great deal of literature describing various processes and process steps, not only sulfonation but also dehydrogenation, alkylation, alkylbenzene distillation and the like. Common sulfonation systems useful herein include sulfuric acid, chlorosulfonic acid, oleum, sulfur trioxide and the like. Sulfur trioxide/air is especially preferred. Details of sulfonation using a suitable air/sulfur trioxide mixture are 15 provided in US 3,427,342, Chemithon. Sulfonation processes are further extensively described in "Sulfonation Technology in the Detergent Industry", W.H. de Groot, Kluwer Academic Publishers, Boston, 1991.

Any convenient workup steps may be used in the present process. Common practice is to neutralize after sulfonation with any suitable alkali. Thus the neutralization step can be conducted 20 using alkali selected from sodium, potassium, ammonium, magnesium and substituted ammonium alkalis and mixtures thereof. Potassium can assist solubility, magnesium can promote soft water performance and substituted ammonium can be helpful for formulating specialty variations of the instant surfactants. The invention encompasses any of these derivative forms of the enhanced alkylbenzene sulfonate surfactant mixtures as produced by the present process and their use in 25 consumer product compositions.

Alternately the acid form of the present surfactants can be added directly to acidic cleaning products, or can be mixed with cleaning ingredients and then neutralized.

The hydrotropes or hydrotrope precursors useful herein can in general be selected from any suitable hydrotrope or hydrotrope precursor, including lower alkyl (C₁-C₈) aromatics and their 30 sulfonic acids and sulfonate salts, but are more typically based on a sulfonic acid or sodium sulfonate salt of toluene, cumene, xylene, napthalene or mixtures thereof. The hydrotrope precursors are selected from any suitable hydrotrope precursor, typically toluene, cumene, xylene, napthalene or mixtures thereof. A hydrotrope precursor is a compound that during step (III), namely the sulfonation step, is converted into a hydrotrope.

Moreover, it is contemplated that the alkylation "step" (I) herein can be "staged" so that two or more reactors operating under different conditions in the defined ranges may be useful. By operating a plurality of such reactors, it is possible to allow for material with less preferred 2-methyl-2-phenyl index to be initially formed and, surprisingly, to convert such material into material with a more preferred 2-methyl-2-phenyl index.

In terms of sulfonating agent selection, the invention encompasses an enhanced alkylbenzene sulfonate surfactant mixture wherein step (II) is performed using a sulfonating agent selected from the group consisting of sulfur trioxide, sulfur trioxide/air mixtures, and sulfuric acid (including oleum). Chlorosulfonic acid or other known sulfonating agents, while less commercially relevant, are also useful and are included for use in the invention.

Although in general, neutralization step (III) can be carried out with any suitable alkali, the invention includes an enhanced alkylbenzene sulfonate surfactant mixture wherein said step (III) is performed using a basic salt, said basic salt having a cation selected from the group consisting of alkali metal, alkaline earth metal, ammonium, substituted ammonium, and mixtures thereof and an anion selected from hydroxide, oxide, carbonate, silicate, phosphate, and mixtures thereof. Preferred basic salt is selected from the group consisting of sodium hydroxide, sodium silicate, potassium hydroxide, potassium silicate, magnesium hydroxide, ammonium hydroxide, and mixtures thereof.

Alkylation Catalyst

To secure the enhanced alkylbenzene sulfonate surfactant mixtures of the invention, the present invention uses a particularly defined alkylation catalyst. Said alkylation catalyst is an intermediate acidity solid porous alkylation catalyst defined in detail hereinafter. Particularly preferred alkylation catalysts comprise at least partially dealuminized acidic non-fluoridated mordenites, at least partially dealuminized acidic fluoridated mordenites, and mixtures thereof. In additional embodiments, a preferred alkylation catalyst is that which exhibits the same or similar characteristics as the mordenite catalyst, under the same or similar conditions. One such catalyst may stem from the group consisting of zeolite beta catalysts, of certain and specific form, but is not preferred.

Numerous alkylation catalysts are unsuitable for making the present enhanced alkylbenzene mixtures and enhanced alkylbenzene sulfonate surfactant mixtures. Unsuitable alkylation catalysts include any of: sulfuric acid, aluminum chloride, and HF. Also unsuitable are non-acidic calcium mordenite, and many others. Other catalysts, such as the DETAL® process catalysts of UOP are also unsuitable, at least in their current commercial executions.

In contrast, suitable alkylation catalysts herein are selected from shape-selective moderately acidic alkylation catalysts, preferably zeolitic. The zeolite catalyst used for the alkylation step (I) is preferably selected from the group consisting of mordenite, HZSM-12, NES and offretite, any of these being in at least partially acidic form. Mixtures can be used and the catalysts can be combined with binders etc. More preferably, the zeolite is substantially in acid form and is contained in a catalyst pellet comprising a conventional binder and further wherein said catalyst pellet comprises at least about 1 %, more preferably at least 5%, more typically from 50% to about 90%, of said zeolite.

More generally, a suitable alkylation catalyst is typically at least partially crystalline, more preferably substantially crystalline not including binders or other materials used to form catalyst pellets, aggregates or composites. Moreover the catalyst is typically at least partially acidic. Fully exchanged Ca-form mordenite, for example, is unsuitable whereas H-form mordenite is suitable.

EP 466,558 describes an acidic mordenite type alkylation catalyst also of possible use herein having overall Si/Al atomic ratio of 15-85 (15-60), Na weight content is less than 1000 ppm (preferably less than 250 ppm), and there is a low or zero content of extra-network Al species; the elementary mesh volume as defined in EP 466,558 is below 2,760 nm³.

US 5,057,472 is likewise useful for preparing alkylation catalysts herein and relates to concurrent dealumination and ion-exchange of an acid-stable Na ion-containing zeolite, preferably mordenite, effected by contact of the zeolite with a 0.5-3 (preferably 1-2.5) M HNO₃ solution containing sufficient NH₄NO₃ to fully exchange the Na⁺ ions for NH₄⁺ and H⁺ ions. The resulting zeolites can have a SiO₂:Al₂O₃ ratio of 15:1 to 26:1, preferably 17:1 to 23:1, and are preferably calcined to at least partially convert the NH₄⁺/H⁺ form to the H⁺ form. Optionally, though not necessarily particularly desirable in the present invention, the catalyst can contain a Group VIII metal (and optionally also an inorganic oxide) together with the calcined zeolite of '472.

Another acidic mordenite catalyst useful for the alkylation step herein is disclosed in US 4,861,935 which relates to a hydrogen form of mordenite incorporated with alumina, the composition having a surface area of at least 580 m² /g. Other acidic mordenite catalysts useful for the alkylation step herein include those described in US 5,243,116 and US 5,198,595. Yet another alkylation catalyst useful herein is described in US 5,175,135 which is an acid mordenite zeolite having a silica/alumina molar ratio of at least 50:1, a Symmetry Index of at least 1.0 as determined by X-ray diffraction analysis, and a porosity such that the total pore volume is in the

range from about 0.18 cc/g to about 0.45 cc/g and the ratio of the combined meso- and macropore- volume to the total pore volume is from about 0.25 to about 0.75.

Particularly preferred alkylation catalysts herein include the acidic mordenite catalysts ZeocatTM FM-8/25H available from Zeochem; CBV 90 A available from Zeolyst International, 5 and LZM-8 available from UOP Chemical Catalysts as well as fluoridated versions of the above commercial catalysts. Fluoridated mordenites can be prepared by a number of ways. A method of providing a particularly useful fluoridated mordenite is described in US 5,777,187. The invention encompasses preferred embodiments in which the mordenites are fluoridated, but also has other preferred embodiments in which the mordenites are non-fluoridated.

10 Most generally, any alkylation catalyst may be used herein provided that the alkylation catalyst can (a) accommodate methyl-substituted olefins as described elsewhere herein into the smallest pore diameter of said catalyst and (b) selectively alkylate benzene with said substituted olefins and optionally mixtures thereof with linear olefins. Acceptable selectivity is in accordance with a 2/3-Phenyl index of about 275 to about 10,000 as defined herein.

15 In other terms, the catalyst selections herein are made in part with the intention of minimizing internal alkylbenzene formation (e.g., 4-phenyl, 5-phenyl ...). The formulators contributing to the present invention have unexpectedly discovered that control of internal alkylbenzene sulfonate isomers in the present inventive surfactant mixtures in conjunction with introduction of limited methyl branching is very helpful for improving their performance. The 20 present invention connects this discovery to discoveries of the synthesis chemists in the present invention, who have determined how to control internal isomer content while providing limited methyl branching in the enhanced alkylbenzene sulfonate surfactant mixtures in accordance with the formulators' prescriptions.

25 The extent to which internal isomer content needs to be controlled can vary depending on the consumer product application and on whether outright best performance or a balance of performance and cost is required. In absolute terms, the amount of internal isomer such as internal alkylbenzene isomer is preferably always kept below 25% by weight, but for best results, from 0 to 10%, preferably less than about 5% by weight. "Internal alkylbenzene" isomers as defined herein include alkylbenzenes having phenyl attachment to an aliphatic chain in the 4,5,6 or 7 30 position.

Without intending to be limited by theory, there are two reasons for which it is believed that the preferred alkylation catalysts are the above-described shape selective zeolitic type catalysts, especially mordenites. The first reason is to provide the selectivity of formation of preferred compounds such as substituted and unsubstituted 2-phenyl and 3-phenylalkylbenzenes.

This selectivity is measured by the 2/3-phenyl index. The second reason is to control the amount of quaternary alkylbenzenes and thus quaternary alkylbenzene sulfonates.

Results with alkylation catalysts such as HF can give quite high levels of quaternary alkylbenzenes as shown in the literature (see J. Org. Chem. Vol. 37, No. 25, 1972). This contrasts 5 with the surprising discovery as part of the present invention that one can attain low levels of quaternary alkylbenzenes in catalyzed reactions of benzene with substituted olefins, as characterized by 2-methyl-2-phenyl index. In practice, some isomerization of the enhanced alkylbenzenes may occur during alkylation, i.e. the ratio of enhanced alkylbenzenes to modified unsubstituted alkylbenzenes may vary.

10 **Second Embodiment:**

Detergent Compositions

The present invention has numerous detergent composition embodiments, which may be in various physical forms, including the detergent composition comprising: (a) from about 1% to about 50%, preferably from about 2% to about 30%, by weight of enhanced alkylbenzene sulfonate surfactant mixture according to the first embodiment, wherein said enhanced alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than about 0.3, preferably of from 0 to 0.2, more preferably no more than about 0.1, more preferably still, no more than about 0.05; (b) from about 0.000001% to about 10%, preferably from about 0.01% to about 2%, of a member selected from the group consisting of optical brighteners, dyes, 15 photobleaches, hydrophobic bleach activators and transition metal bleach catalysts, preferably at least two of said member components, more preferably at least two of said member components including an optical brightener as one of the member components; (c) from 0.1% to about 40% by weight (preferably not more than about 30%) of surfactants selected from the group consisting of cationic surfactants, nonionic surfactants, anionic surfactants, and amine oxide surfactants (more 20 preferably at least one cationic surfactant is present at a level of from about 0.2% to about 5% by weight, or at least one nonionic surfactant is present at a level of from about 0.5% to about 25% by weight, or at least one alkyl sulfate surfactant or alkyl(polyalkoxy)sulfate surfactant is present at a level of from about 0.5% to about 25% by weight); and (d) from about 10% to about 99% of 25 conventional cleaning adjuncts (other than any of (a) - (c)); provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said enhanced alkylbenzene sulfonate surfactant mixture (for example as a result of blending into the detergent composition one or more commercial, especially linear, typically linear C₁₀-C₁₄, alkylbenzene sulfonate surfactants), said detergent composition is further characterized by an overall 2/3-phenyl index of at least about 200, preferably at least about 250, more preferably at least about 350, more 30

preferably still, at least about 500, wherein said overall 2/3-phenyl index is determined by measuring 2/3-phenyl index, as defined herein, on a blend of said enhanced alkylbenzene sulfonate surfactant mixture and said any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of 5 said enhanced alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition; and further provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said enhanced alkylbenzene sulfonate surfactant mixture (for example as a result of blending into the detergent composition one or more commercial, especially linear, typically 10 linear C_{10} - C_{14} , alkylbenzene sulfonate surfactants), said detergent composition is further characterized by an overall 2-methyl-2-phenyl index of less than about 0.3, preferably from 0 to 0.2, more preferably no more than about 0.1, more preferably still, no more than about 0.05, wherein said overall 2-methyl-2-phenyl index is to be determined by measuring 2-methyl-2-phenyl index, as defined herein, on a blend of said enhanced alkylbenzene sulfonate surfactant 15 mixture and any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of said enhanced alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition.

These provisions may appear somewhat unusual, however they are consistent with the 20 spirit and scope of the present invention, which encompasses a number of economical but less preferred approaches in terms of overall cleaning performance, such as blending of the enhanced alkylbenzene sulfonate surfactants with conventional linear alkylbenzene sulfonate surfactants either during synthesis or during formulation into the detergent composition. Moreover, as is well known to practitioners of detergent analysis, a number of detergent adjuncts (paramagnetic 25 materials such as certain transition metal bleach catalysts, for example, and sometimes even water) are capable of interfering with methods for determining the parameters of alkylbenzene sulfonate surfactant mixtures as described hereinafter. Hence wherever possible, analysis should be conducted on dry materials before mixing them into the detergent compositions.

Numerous variations of the present detergent compositions are useful. Such variations 30 may include detergent compositions which are substantially free from alkylbenzene sulfonate surfactants other than said enhanced alkylbenzene sulfonate surfactant mixture of the present invention; and/or which may comprise, in said component (c), at least about 0.1%, preferably no more than about 10%, more preferably no more than about 5%, more preferably still, no more than about 1%, of a commercial C_{10} - C_{14} linear alkylbenzene sulfonate surfactant; and/or which

may comprise other types of conventional surfactants (i.e., cationic, nonionic, zwitterionic, anionic etc.)

Further the present invention includes a detergent composition comprising (preferably consisting essentially of): (a) from about 0.1% to about 95%, by weight (preferably from about 5% to about 50%, more preferably from about 1%, preferably at least 2%, more preferably at least 4%, more preferably at least 6%, more preferably still at least 8% to about 35%) of enhanced alkylbenzene sulfonate surfactant mixture according to the invention; (b) from about 0.00001% to about 99.9% (preferably from about 5% to about 98%, more preferably from about 50% to about 95%) of conventional cleaning adjuncts other than surfactants; and (c) from 0% to about 50%, by weight (in some preferred embodiments, 0%, and in others preferably from about 0.1% to about 30%, more typically from about 0.2% to about 10%), of a surfactant other than said enhanced alkylbenzene sulfonate surfactant mixture; provided that when said detergent composition comprises any other alkylbenzene sulfonate than the alkylbenzene sulfonate of said enhanced alkylbenzene sulfonate surfactant mixture, said enhanced alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate, as a mixture, have an overall 2/3-phenyl index of from about 275 to 10,000, preferably from about 300 to about 5,000, more preferably from about 325 to about 2,5000.

In another detergent embodiment, there is encompassed herein a detergent composition comprising: (a) from about 0.1% to about 95%, by weight (preferably from about 0.5% to about 50%, more preferably from about 1% to about 35%) of enhanced alkylbenzene sulfonate surfactant mixture of the invention; (b) from about 0.00001% to about 99.9% (preferably from about 5% to about 98%, more preferably from about 50% to about 95%) of conventional cleaning adjuncts other than surfactants; and (c) from 0.1% to about 50%, by weight (preferably from about 0.1% to about 35%, more typically from about 1% to about 15%) of surfactants other than alkylbenzene sulfonates (preferably, one or more surfactants selected from the group consisting of cationic surfactants, anionic surfactants, and anionic surfactants other than alkylbenzene sulfonates, more preferably wherein a cationic surfactant is present, said cationic surfactant is at a level of from about 0.2% to about 5%).

The invention also includes a detergent composition consisting essentially of: (a) from about 1% to about 50% (preferably from about 1% to about 35%), by weight of enhanced alkylbenzene sulfonate surfactant mixture according to the first embodiment of the invention; (b) from about 0.00001% to about 99.9% (preferably from about 5% to about 98%, more preferably from about 50% to about 95%) of conventional cleaning adjuncts other than surfactants; and (c) from 0.1% to about 50% (preferably from about 0.1% to about 35%, more typically from about

1% to about 15%) by weight of surfactants other than alkylbenzene sulfonates (preferably, one or more surfactants selected from the group consisting of cationic surfactants, anionic surfactants, and anionic surfactants other than alkylbenzene sulfonates, more preferably wherein a cationic surfactant is present at a level of from about 0.2% to about 5%); and (d) from 0.1% to about 95% water.

5 Likewise part of the invention is a detergent composition consisting essentially of: (a) from about 0.1% to about 95%, by weight of enhanced alkylbenzene sulfonate surfactant mixture according to the first embodiment; and

(b) from about 0.00001% to about 99.9% of conventional cleaning adjuncts other than surfactants.

10 More generally, detergent compositions can include the enhanced alkylbenzene sulfonate surfactant mixtures together with any conventional cleaning adjunct other than surfactants, such as those wherein the adjunct is selected from the group consisting of builders, deterutive enzymes, bleaching systems, brighteners, at least partially water-soluble or water dispersible polymers, abrasives, bactericides, tarnish inhibitors, dyes, solvents, hydrotropes, perfumes, thickeners, 15 antioxidants, processing aids, suds boosters, suds suppressors, buffers, anti-fungal agents, mildew control agents, insect repellents, anti-corrosive aids, chelants and mixtures thereof.

The compositions in accordance with the invention can take a variety of physical forms including granular, gel, tablet, bar and liquid forms. The compositions include the so-called concentrated granular detergent compositions adapted to be added to a washing machine by 20 means of a dispensing device placed in the machine drum with the soiled fabric load.

The mean particle size of the components of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

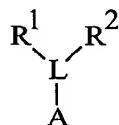
25 The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

30 Certain preferred granular detergent compositions in accordance with the present invention are the high-density types, now common in the marketplace; these typically have a bulk density of at least 600 g/litre, more preferably from 650 g/litre to 1200 g/litre. Such high-density types may be made by any suitable known process.

Third Embodiment:

Precursor Alkylbenzene Mixtures

The present invention also includes an enhanced alkylbenzene mixture comprising (preferably consisting essentially of): (a) from about 60% to about 25%, preferably from about 55% to about 35%, more preferably from about 50% to 40%, by weight of a mixture of enhanced alkylbenzenes having formula (I):



5

(I)

wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen and having two methyl termini, and wherein said mixture of enhanced alkylbenzenes contains two or more compounds of said formula (I) differing in molecular weight and wherein said mixture of enhanced alkylbenzenes is characterized by a sum of carbon atoms in R¹, R² and L of from 9 to 15, preferably from 10 to 14; and an average aliphatic carbon content (i.e., excluding A), based on the sum of R¹, L and R², of from about 10.0 to about 14.0, preferably from about 10.5 to about 12.5, more preferably from about 11.0 to about 12.0 carbon atoms; and further, wherein L has no substituents other than A, R¹ and R²; R¹ is C₁-C₃ alkyl (preferably C₁-C₂ alkyl, more preferably methyl); R² is selected from H and C₁-C₃ alkyl (preferably H and C₁-C₂ alkyl, more preferably H and methyl provided that in at least about 0.5, more preferably 0.7, more preferably 0.9 to 1.0 mole fraction of said enhanced alkylbenzenes, R² is H); A is a (nonsulfonated) benzene moiety (C₆H₅- having no substituents other than L); and (b) from about 40% to about 75%, preferably from about 45% to about 65%, more preferably from about 50% to 60%, by weight of a mixture of modified unsubstituted alkylbenzenes having formula (II):

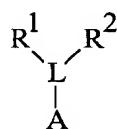


(II)

wherein A is a (nonsulfonated) benzene moiety (C₆H₅- having no substituents other than L) and Y is a linear aliphatic moiety with no substituents other than A consisting of carbon and hydrogen having two methyl termini, and wherein Y has from 9 to 15 carbon atoms in total (preferably from 10 to 14) and said mixture of modified unsubstituted alkylbenzenes has an average aliphatic carbon content (i.e., carbon content excluding A) of from about 10.0 to about 14.0 carbon atoms, preferably from about 10.5 to about 12.5 carbon atoms, more preferably from about 11.0 to about 12.0 carbon atoms; and wherein said modified unsubstituted alkylbenzene mixture is further characterized by a 2/3-phenyl index of from about 275 to about 10,000, more preferably from

about 300 to about 5,000, more preferably still from about 325 to about 2,500, and a 2-methyl-2-phenyl index of less than about 0.3, preferably from 0 to about 0.2, more preferably no more than about 0.1, more preferably still, 0.05 or less.

In another example, the invention includes an enhanced alkylbenzene mixture comprising: 5 I) from 20% to about 99%, (or more, preferably 40% or more, more preferably more than half, e.g., 60% or more, more preferably still 70% or more), by weight of a first alkylbenzene mixture, wherein said first alkylbenzene mixture is said enhanced alkylbenzene mixture and consists essentially of: a) from about 60% to about 25% by weight of a mixture of enhanced alkylbenzenes having formula (I):



10

(I)

wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen and having two methyl termini, and wherein said mixture of enhanced alkylbenzenes contains two or more compounds of said formula (I) differing in molecular weight and wherein said mixture of enhanced alkylbenzenes is characterized by a sum of carbon atoms in R¹, R² and L of from 9 to 15, preferably from 10 to 14; and an average aliphatic carbon content, based on the sum of R¹, L and R², of from about 10.0 to about 14.0, preferably from about 10.5 to about 12.5, more preferably from about 11.0 to about 12.0 carbon atoms; and further, wherein L has no substituents other than A, R¹ and R²; R¹ is C₁-C₃ alkyl (preferably C₁-C₂ alkyl, more preferably methyl); R² is selected from H and C₁-C₃ alkyl (preferably H and C₁-C₂ alkyl, more preferably H and methyl, more preferably H and methyl provided that in at least about 0.5, more preferably 0.7, more preferably 0.9 to 1.0 mole fraction of said enhanced alkylbenzene sulfonates, R² is H); A is a (nonsulfonated) benzene moiety (C₆H₅- having no substituents other than L); and b) from about 40% to about 75% by weight (preferably from about 45% to about 65%, more preferably from about 50% to about 60%) of a mixture of modified unsubstituted alkylbenzenes having formula 15 (II):



(II)

wherein A is a (nonsulfonated) benzene moiety (C₆H₅- having no substituents other than A) and Y is a linear aliphatic moiety having no substituents other than A consisting of carbon and hydrogen

having two methyl termini, and wherein Y has from 9 to 15, preferably from 10 to 14 carbon atoms in total and said mixture of modified unsubstituted alkylbenzenes has an average aliphatic carbon content of from about 10.0 to about 14.0, preferably from about 10.5 to about 12.5, more preferably from about 11.0 to about 12.0 carbon atoms; wherein said first alkylbenzene mixture 5 has a 2/3-phenyl index of from about 275 to about 10,000, more preferably from about 300 to about 5,000, more preferably at least about 325 to about 2,500; and II) the balance, no more than about 80%, (preferably no more than about 60%, more preferably less than half, e.g., no more than about 40%, more preferably still no more than about 25%), by weight of a second alkylbenzene mixture, wherein said second alkylbenzene mixture has a 2/3-phenyl index of from 10 about 75 to about 160 (typical of current commercial LAB); and wherein said enhanced alkylbenzene mixture has an overall 2/3-phenyl index of from about 155 to about 10,000 (preferably from about 170 to about 1200, more preferably from about 180 to about 700).

Other Embodiments:

Medium 2/3-Phenyl Surfactant Mixtures

15 The present invention also encompasses enhanced alkylbenzene sulfonate surfactant mixtures that are more particularly termed "medium 2/3-phenyl surfactant mixtures". Such mixtures are not the most preferred offered by the invention, but can be very economical.

Thus the invention includes a medium 2/3-phenyl surfactant mixture consisting essentially of: from 1% (preferably at least about 5%, more preferably at least about 10 %) to about 60% (in one mode preferably less than about 50%, more preferably less than about 40 %), by weight of a first alkylbenzene sulfonate surfactant, wherein said first alkylbenzene sulfonate surfactant is an enhanced alkylbenzene sulfonate surfactant mixture according to the first embodiment; and from 40% (in one mode preferably at least about 50%, more preferably at least about 60 %) to about 99% (preferably less than about 95%, more preferably less than about 90%), by weight of a second alkylbenzene sulfonate surfactant, wherein said second alkylbenzene sulfonate surfactant is an alkylbenzene sulfonate surfactant mixture other than said enhanced alkylbenzene sulfonate surfactant mixture according to the first embodiment, and wherein said second alkylbenzene sulfonate surfactant has a 2/3-phenyl index of from about 75 to about 160 (typically said second alkylbenzene sulfonate surfactant is a commercial C₁₀-C₁₄ linear alkylbenzene sulfonate surfactant, e.g., DETAL ® process LAS or HF process LAS though in general any commercial linear (LAS) or branched (ABS, TPBS) type can be used); provided that said medium 2/3-phenyl surfactant mixture has a 2/3-phenyl index of from about 160 to about 275 (preferably from about 170 to about 265, more preferably from about 180 to about 255). (of course it is equally possible within the spirit and scope of the invention to prepare any blend of

the enhanced alkylbenzene sulfonate surfactant mixture of the invention with any known commercial linear or branched alkylbenzene sulfonate surfactant.

Also included is a detergent composition comprising (preferably consisting essentially of): (a) from about 0.1% to about 95%, by weight (preferably from about 0.5% to about 50%, more preferably from about 1% to about 35%) of medium 2/3-phenyl surfactant mixture as defined supra; (b) from about 0.00001% to about 99.9% (preferably from about 5% to about 98%, more preferably from about 50% to about 95%) of conventional cleaning adjuncts other than surfactants; and (c) from 0% to about 50%, by weight (in some preferred embodiments, 0%, and in others preferably from about 0.1% to about 30%, more typically from about 0.2% to about 10%), of a surfactant other than said medium 2/3-phenyl surfactant mixture; provided that when said detergent composition comprises any other alkylbenzene sulfonate than the alkylbenzene sulfonate of said medium 2/3-phenyl surfactant mixture, said medium 2/3-phenyl surfactant mixture and said other alkylbenzene sulfonate, as a mixture, have an overall 2/3-phenyl index of from about 160 to about 275 (preferably from about 170 to about 265, more preferably from about 180 to about 255).

Likewise part of the invention is a detergent composition comprising:

(a) from about 0.1% to about 95%, by weight of medium 2/3-phenyl surfactant mixture as defined supra; (b) from about 0.00001% to about 99.9% of conventional cleaning adjuncts other than surfactants; and (c) from 0.1% to about 50%, by weight of surfactants other than alkylbenzene sulfonates (preferably, one or more surfactants selected from the group consisting of cationic surfactants, anionic surfactants, and anionic surfactants other than alkylbenzene sulfonates, more preferably wherein a cationic surfactant is present at a level of from about 0.2% to about 5%).

Moreover there is included herein a detergent composition consisting essentially of: (a) from about 1% to about 50%, by weight of medium 2/3-phenyl surfactant mixture as defined supra; (b) from about 0.1% to about 98.8% of conventional cleaning adjuncts other than surfactants; (c) from 0.1% to about 50%, by weight of surfactants other than alkylbenzene sulfonates (preferably, one or more surfactants selected from the group consisting of cationic surfactants, anionic surfactants, and anionic surfactants other than alkylbenzene sulfonates, more preferably wherein a cationic surfactant is present at a level of from about 0.2% to about 5%); and (d) from about 0.1% to about 98.8% water.

In additional embodiments of the medium 2/3-phenyl type, there is included a detergent composition consisting essentially of: (a) from about 0.1% to about 95%, preferably from 1% to about 50% by weight of medium 2/3-phenyl surfactant mixture as defined supra; and (b) from about 0.00001% to about 99.9% of conventional cleaning adjuncts other than surfactants.

Processes for preparing a medium 2/3-phenyl surfactant mixture include those comprising a step selected from: (i) blending said first alkylbenzene sulfonate surfactant and said second alkylbenzene sulfonate surfactant; and (ii) blending the nonsulfonated precursor of said first alkylbenzene sulfonate surfactant and the nonsulfonated precursor of said second alkylbenzene sulfonate surfactant and sulfonating said blend.

Preparative Examples

EXAMPLE 1

Mixture of 4-methyl-4-nonanol, 5-methyl-5-decanol, 6-methyl-6-undecanol and 6-methyl-6-dodecanol (A starting-material for methyl-substituted olefins)

10 A mixture of 4.01 g of 2-pentanone, 32.70 g of 2-hexanone, 45.41 g of 2-heptanone, 17.88 g of 2-octanone and 72.6 g of diethyl ether is added to an addition funnel. The ketone mixture is then added dropwise over a period of 2.25 hours to a nitrogen blanketed stirred three neck 2 L round bottom flask, fitted with a reflux condenser and containing 612 mL of 2.0 M n-pentylmagnesium bromide in diethyl ether and an additional 400 mL of diethyl ether. After the addition is complete 15 the reaction mixture is stirred an additional 2.5 hours at 20°C. The reaction mixture is then added to 1kg of cracked ice with stirring. To this mixture is added 401.2 g of 30% sulphuric acid solution. The aqueous acid layer is drained and the remaining ether layer is washed twice with 750 mL of water. The ether layer is then evaporated under vacuum to yield 179.6 g of a mixture of 4-methyl-4-nonanol, 5-methyl-5-decanol, 6-methyl-6-undecanol and 6-methyl-6-dodecanol.

EXAMPLE 2

Substantially Methyl-substituted Olefin Mixture with Randomized Branching (A methyl-substituted olefin mixture, which is an alkylating agent for preparing enhanced alkylbenzenes in accordance with the invention)

20 a) A 179.6 g sample of the mono methyl branched alcohol mixture of Example 1 is added to a nitrogen blanketed stirred three neck round bottom 500 mL flask, fitted with a Dean Stark trap and a reflux condenser along with 36.5 g of a shape selective zeolite catalyst (acidic mordenite catalyst Zeocat™ FM-8/25H). With mixing, the mixture is then heated to about 110-155°C and water and some olefin is collected over a period of 4-5 hours in the Dean Stark trap. The conversion of the alcohol mixture of Example 1 to a substantially non-randomized methyl branched olefin mixture is now complete. The substantially non-randomized methyl branched olefin mixture remaining in the flask along with the substantially non-randomized methyl branched olefin mixture collected in the dean stark trap is recombined and filtered to remove catalyst. The solid filter cake is washed twice with 100 mL portions of hexane. The hexane

filtrate is evaporated under vacuum and the resulting product is combined with the first filtrate to give 151.2 g of a substantially non-randomized methyl branched olefin mixture.

5 b) The olefin mixture of Example 2a is combined with 36g of a shape selective zeolite catalyst (acidic mordenite catalyst Zeocat™ FM-8/25H) and reacted according to Example 2a with the following changes. The reaction temperature is raised to 190-200°C for a period of about 1-2 hours to randomize the specific branch positions in the olefin mixture. The substantially mono methyl branched olefin mixture with randomized branching remaining in the flask along with the substantially mono methyl branched olefin mixture with randomized branching collected in the dean stark trap are recombined and filtered to remove catalyst. The solid filter cake is washed 10 twice with 100 mL portions of hexane. The hexane filtrate is evaporated under vacuum and the resulting product is combined with the first filtrate to give 150.0 g of a substantially mono methyl branched olefin mixture with randomized branching.

EXAMPLE 3

Enhanced Alkylbenzenes with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl index of about 0.02 (Enhanced alkylbenzenes in accordance with the invention)

15.0 g of the substantially mono methyl branched olefin mixture of Example 2 and 36 g of a shape selective zeolite catalyst (acidic mordenite catalyst Zeocat™ FM-8/25H) are added to a 2-gallon stainless steel, stirred autoclave. Residual olefin and catalyst in the container are washed into the autoclave with 300 mL of n-hexane and the autoclave is sealed. From outside the 20 autoclave cell, 2000 g of benzene (contained in a isolated vessel and added by way of an isolated pumping system inside the isolated autoclave cell) is added to the autoclave. The autoclave is purged twice with 250 psig N₂, and then charged to 60 psig N₂. The mixture is stirred and heated to about 200°C for about 4-5 hours. The autoclave is cooled to about 20°C overnight. The valve is opened leading from the autoclave to the benzene condenser and collection tank. The autoclave 25 is heated to about 120°C with continuous collection of benzene. No more benzene is collected by the time the reactor reaches 120°C. The reactor is then cooled to 40°C and 750 g of n-hexane is pumped into the autoclave with mixing. The autoclave is then drained to remove the reaction mixture. The reaction mixture is filtered to remove catalyst and the n-hexane is removed under vacuum. The product is distilled under vacuum (1-5 mm of Hg). The enhanced alkylbenzenes 30 with a 2/3-Phenyl index of about 550 and a 2-methyl-2-phenyl index of about 0.02 is collected from 76°C - 130°C (170 g).

EXAMPLE 4

Enhanced Alkylbenzene sulfonic Acids with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl Index of about 0.02 (Enhanced alkylbenzene sulfonic acids in accordance with invention)

5 The product of Example 3 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed to give 214 g of an enhanced alkylbenzene sulfonic acids with a 2/3-Phenyl index of about 550 and a 2-methyl-2-phenyl index of about 0.02

EXAMPLE 5

**Enhanced Alkylbenzene sulfonate, Sodium Salts with a 2/3-Phenyl index of about 550
(Enhanced alkylbenzene sulfonate surfactants in accordance with the invention)**

The product of Example 4 is neutralized with a molar equivalent of sodium methoxide in methanol and the methanol is evaporated to give 229 g of an enhanced alkylbenzene sulfonate, sodium salts with a 2/3-Phenyl index of about 550 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 6

15 **Enhanced Alkylbenzene Mixture according to the invention with a 2/3-Phenyl Index of
about 550 and a 2-Methyl-2-Phenyl Index of about 0.02
(Enhanced and Modified Unsubstituted Alkylbenzene Mixture)**

66.15 g of the substantially mono methyl branched olefin mixture of Example 2, 80.85 g a nonbranched olefin mixture (decene: undecene: dodecene: tridecene ratio of 17: 38: 35: 10) and 20 36 g of a shape selective zeolite catalyst (acidic mordenite catalyst ZeocatTM FM-8/25H) are added to a 2-gallon stainless steel, stirred autoclave. Residual olefin and catalyst in the container are washed into the autoclave with 300 mL of n-hexane and the autoclave is sealed. From outside the autoclave cell, 2000 g of benzene (contained in a isolated vessel and added by way of an isolated pumping system inside the isolated autoclave cell) is added to the autoclave. The 25 autoclave is purged twice with 250 psig N₂, and then charged to 60 psig N₂. The mixture is stirred and heated to about 200°C for about 4-5 hours. The autoclave is cooled to about 20°C overnight. The valve is opened leading from the autoclave to the benzene condenser and collection tank. The autoclave is heated to about 120°C with continuous collection of benzene. No more benzene is collected by the time the reactor reaches 120°C. The reactor is then cooled to 30 40°C and 750 g of n-hexane is pumped into the autoclave with mixing. The autoclave is then drained to remove the reaction mixture. The reaction mixture is filtered to remove catalyst and the n-hexane is removed under vacuum. The product is distilled under vacuum (1-5 mm of Hg). An enhanced alkylbenzene mixture with a 2/3-Phenyl index of about 550 and a 2-methyl-2-phenyl index of about 0.02 is collected from 76°C - 130°C (167 g).

EXAMPLE 7**Enhanced Alkylbenzene Sulfonic Acid Mixture according to the invention****with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl Index of about 0.02****(Enhanced and modified unsubstituted alkylbenzene sulfonic acid mixture)**

5 100 g of the product of Example 6 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed to give 135.8 g of an enhanced alkylbenzene sulfonic acid mixture with a 2/3-Phenyl index of about 550 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 8

10 **Enhanced Alkylbenzene Sulfonate, Sodium Salt Mixture According to the invention with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl Index of about 0.02**

(Enhanced and Modified Unsubstituted Alkylbenzene Sulfonate, Sodium Salt Mixture)

15 The enhanced sulfonic acid mixture of Example 7 is neutralized with a molar equivalent of sodium methoxide in methanol and the methanol is evaporated to give 225 g of an enhanced alkylbenzene sulfonate, sodium salt mixture with a 2/3-Phenyl index of about 550 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 9**Enhanced alkylbenzene sulfonate surfactant mixtures according to the invention****(Medium 2/3-phenyl type)**

20 Blends are prepared of:

I) Enhanced alkylbenzene sulfonate surfactant mixture in accordance with the invention having a 2/3-Phenyl index of about 550 (according to Example 8)
 II) Commercial C_{11.7} (average) linear alkylbenzene sulfonate surfactant (HF type) sodium salt having a 2/3-Phenyl index of about 100

25 In the table below, percentages are by weight:

	A	B	C
I	25%	15%	38%
II	75%	85%	62%

Each of the above blends has a 2/3-phenyl index in the range from about 160 to about 275.

EXAMPLE 10**Enhanced Alkylbenzene sulfonate surfactant mixtures according to the invention****(Medium 2/3-phenyl type)**

30 Blends are prepared of:

I) Enhanced alkylbenzene sulfonate surfactant mixture in accordance with the invention having a 2/3-Phenyl index of about 550 (according to Example 8)

II) Commercial C_{11.7} (average) linear alkylbenzene sulfonate surfactant (DETAL ® type) sodium salt having a 2/3-Phenyl index of about 150

5 In the table below, percentages are by weight:

	A	B	C
I	25%	15%	10%
II	75%	85%	90%

Each of the above blends has a 2/3-phenyl index in the range from about 160 to about 275.

EXAMPLE 11

Enhanced Alkylbenzene sulfonic acid mixtures according to the invention (Medium 2/3-phenyl type)

10 Blends are prepared of:

I) Enhanced alkylbenzene sulfonic acid surfactant mixture in accordance with the invention having a 2/3-Phenyl index of about 550 (according to Example 7)

II) Commercial C_{11.7} (average) linear alkylbenzene sulfonic acid (HF type) having a 2/3-Phenyl index of about 100.

15 In the table below, percentages are by weight:

	A	B	C
I	25%	15%	38%
II	75%	85%	62%

Each of the above blends has a 2/3-phenyl index in the range from about 160 to about 275.

EXAMPLE 12

Enhanced Alkylbenzene sulfonic acid mixtures according to the invention (Medium 2/3-phenyl type)

20 Blends are prepared of:

I) Enhanced alkylbenzene sulfonic acid mixture in accordance with the invention having a 2/3-Phenyl index of about 550 (according to Example 4)

25 II) Commercial C_{11.7} (average) linear alkylbenzene sulfonic acid (DETAL ® type) having a 2/3-Phenyl index of about 150.

In the table below, percentages are by weight:

	A	B	C
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I	25%	15%	10%
II	75%	85%	90%

Each of the above blends has a 2/3-phenyl index in the range from about 160 to about 275.

EXAMPLE 13

**Enhanced Alkylbenzene mixtures according to the invention
(Medium 2/3-phenyl type)**

5 Blends are prepared of:

- I) Enhanced alkylbenzene mixture in accordance with the invention having a 2/3-Phenyl index of about 550 (according to Example 6)
- II) Commercial C_{11.7} (average) linear alkylbenzene (HF type) having a 2/3-Phenyl index of about 100.

10 In the table below, percentages are by weight:

	A	B	C
I	25%	15%	38%
II	75%	85%	62%

Each of the above blends has a 2/3-phenyl index in the range from about 160 to about 275.

EXAMPLE 14

**Enhanced Alkylbenzene mixtures according to the invention
(Medium 2/3-phenyl type)**

15 Blends are prepared of:

- I) enhanced alkylbenzene sulfonate surfactant mixture in accordance with the invention having a 2/3-Phenyl index of about 550 (according to Example 3)
- II) Commercial C_{11.7} (average) linear alkylbenzene (DETAL ® type) having a 2/3-Phenyl index of about 150.

20 In the table below, percentages are by weight:

	A	B	C
I	25%	15%	10%
II	75%	85%	90%

Each of the above blends has a 2/3-phenyl index in the range from about 160 to about 275.

EXAMPLE 15

25 **Enhanced Alkylbenzene Mixture according to the invention with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl Index of about 0.02
(Enhanced and Modified Unsubstituted Alkylbenzene Mixture)**

150 g of an olefin or paraffin mixture with chain length of C₁₀-C₁₃, which is obtained via any one of the following:

5 1) Dehydrogenation of a paraffin mixture obtained from kerosene feed stock via a molecular sieving unit designed to isolate a mixture, consisting mainly of both linear and monomethyl branched paraffins from cyclic and dimethyl branched paraffins with a chain length of C₁₀-C₁₃,

is blended, if needed, to achieve a linear content of 40% to 75% and is converted to an alkylbenzene mixture according to Example 3.

EXAMPLE 16

10 **Enhanced Alkylbenzene Sulfonic Acid Mixture according to the invention with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl Index of about 0.02**
(Enhanced and Modified Unsubstituted Alkylbenzene sulfonic Acid Mixture)

15 10 g of the product of Example 15 is sulfonated with a molar equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride is removed to give 13.58 g of an enhanced alkylbenzene sulfonic acid mixture with a 2/3-Phenyl index of about 550 and a 2-methyl-2-phenyl index of about 0.02.

EXAMPLE 17

20 **Enhanced Alkylbenzene Sulfonate, Sodium Salt Mixture According to the invention with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl Index of about 0.02**
(Enhanced and Modified Unsubstituted Alkylbenzene sulfonate, Sodium Salt Mixture)

The product of Example 16 is converted to it's sodium salt using the procedure of Example 5.

EXAMPLE 18

25 **Enhanced Alkylbenzene Sulfonate, Sodium Salt Mixture according to the invention with a 2/3-Phenyl Index of about 550 and a 2-Methyl-2-Phenyl Index of about 0.02**
(Enhanced and Modified Unsubstituted Alkylbenzene Mixture)

150 g of an olefin mixture with chain length of C₁₀-C₁₃, which is obtained via any one of the following:

30 5) Dimerization of short chain olefin mixtures inside a molecular sieve
6) Oligomerization of short chain olefin mixtures inside a molecular sieve
7) Product of cracking long-chain hydrocarbon waxes under conditions to obtain a mainly mono methyl branched olefin product;
8) Dehydrogenation of a paraffin mixture obtained from a gas to liquids (GTL) plant.

Is blended with linear olefins to provide a linear to branch ratio of about 50:50 then converted to an alkylbenzene mixture according to Example 3, an alkylbenzene sulfonic acid according to the Example 4 and finally converted to a salt of the acid according to Example 5.

EXAMPLE 19

5 **Enhanced Alkylbenzene Sulfonate, Sodium Salt Mixture according to the invention via blending of (I) mono-methyl substituted olefin mixture and (II) linear olefin mixture as defined in the table below.**

Mixture	Blend 1	Blend 2	Blend 3	Blend 4
I	25%	35%	45%	60%
II	75%	65%	55%	40%

10 Each of the four blends above are alkylated according to Example 3, sulfonated according to Example 4, and neutralized according to Example 5.

Methods for Determining Compositional Parameters (2/3-phenyl index, 2-methyl-2-phenyl index) of Mixed Alkylbenzene/ Alkylbenzene sulfonate/ Alkylbenzene sulfonic Acid Systems.

15 It is well known in the art to determine compositional parameters of conventional linear alkylbenzenes and/or highly branched alkylbenzene sulfonates (TPBS, ABS). See, for Example Surfactant Science Series, Volume 40, Chapter 7 and Surfactant Science Series, Volume 73, Chapter 7. Typically, this is done by GC and/or GC-mass spectroscopy for the alkylbenzenes and HPLC for the alkylbenzene sulfonates or sulfonic acids; ¹³C nmr is also commonly used. Another common practice is desulfonation. This permits GC and/or GC-mass spectroscopy to be used, since desulfonation converts the sulfonates or sulfonic acids to the alkylbenzenes that are tractable by such methods.

20 In general, the present invention provides unique and relatively complex mixtures of enhanced alkylbenzenes, and similarly complex surfactant mixtures of enhanced alkylbenzene sulfonates and/or alkylbenzene sulfonic acids. Compositional parameters of such compositions can be determined using variations and combinations of the art-known methods.

25 The sequence of methods to be used depends on the composition to be characterized as follows:

Composition to be characterized	Sequence of Methods (Methods separated by commas are run in sequence, others can be run in parallel)
Alkylbenzene mixtures	GC, NMR1 NMR 2
Alkylbenzene mixtures	GC, DIS, GC, NMR1 NMR 2

with impurities*	
Alkylbenzene sulfonic acid mixtures	Option 1: HPLC, NMR3 NMR 4 Option 2: HPLC, DE, NMR1 NMR 2
Alkylbenzene sulfonate salt mixtures	Option 1: HPLC, AC, NMR3 NMR 4 Option 2: HPLC, DE, NMR1 NMR 2
Alkylbenzene sulfonic acid mixtures with impurities*	Option 1: HPLC, HPLC-P, HPLC, NMR3 NMR 4 Option 2: HPLC, DE, DIS, GC, NMR1 NMR 2
Alkylbenzene sulfonate salt mixtures with impurities*	Option 1: HPLC, HPLC-P, HPLC, AC, NMR3 NMR 4 Option 2: HPLC, DE, DIS, GC, NMR1 NMR 2

* Typically preferred when the material contains more than about 10% impurities such as dialkylbenzenes, olefins, paraffins, hydrotropes, dialkylbenzene sulfonates, etc.

GC

Equipment:

- 5 • Hewlett Packard Gas Chromatograph HP5890 Series II equipped with a split/splitless injector and FID
- J&W Scientific capillary column DB-1HT, 30 meter, 0.25mm id, 0.1um film thickness cat# 1221131
- Restek Red lite Septa 11mm cat# 22306
- 10 • Restek 4mm Gooseneck inlet sleeve with a carbofrit cat# 20799-209.5
- O-ring for inlet liner Hewlett Packard cat# 5180-4182
- J.T.Baker HPLC grade Methylene Chloride cat# 9315-33, or equivalent
- 2ml GC autosampler vials with crimp tops, or equivalent

Sample Preparation:

- 15 • Weigh 4-5 mg of sample into a 2 ml GC autosampler vial
- Add 1 ml J.T. Baker HPLC grade Methylene Chloride, cat# 9315-33 to the GC vial, seal with 11mm crimp vial teflon lined closures (caps), part # HP5181-1210 using crimper tool, part # HP8710-0979 and mix well
- The sample is now ready for injection into the GC

GC Parameters:

Carrier Gas: Hydrogen

Column Head Pressure: 9 psi

Flows: Column Flow @ 1 ml/min.

Split Vent @ ~3ml/min.

Septum Purge @ 1 ml/min.

5 Injection: HP 7673 Autosampler, 10 ul syringe, 1ul injection

Injector Temperature: 350 °C

Detector Temperature: 400 °C

Oven Temperature Program: initial 70 °C hold 1 min.

rate 1 °C/min.

10 final 180 °C hold 10 min.

Standards required for this method are 2-phenyloctane and 2-phenylpentadecane, each freshly distilled to a purity of greater than 98%. Run both standards using the conditions specified above to define the retention time for each standard. This defines a retention time range which is the retention time range to be used for characterizing any alkylbenzenes or alkylbenzene mixtures in the context of this invention (e.g., test samples). Now run the test samples for which compositional parameters are to be determined. Test samples pass the GC test provided that greater than 90% of the total GC area percent is within the retention time range defined by the two standards. Test samples that pass the GC test can be used directly in the NMR1 and NMR2 test methods. Test samples that do not pass the GC test must be further purified by distillation until 20 the test sample passes the GC test.

25 **DESULFONATION (DE)** - The desulfonation method is a standard method described in "The Analysis of Detergents and Detergent Products" by G. F. Longman on pages 197-199. Two other useful descriptions of this standard method are given on page 230-231 of volume 40 of the Surfactant Science Series edited by T. M. Schmitt: "Analysis of Surfactants" and on page 272 of volume 73 of the Surfactant Science Series: "Anionic Surfactants" edited by John Cross. This is an alternative method to the HPLC method, described herein, for evaluation of alkylbenzene sulfonic acid and/or salt mixtures (alkylbenzene sulfonic acid and/or salt mixtures, including those of the claimed invention). The method provides a means of converting the sulfonic acid and/or salt mixture into alkylbenzene mixtures which can then be analyzed by means of the GC and NMR methods NMR1 and NMR2 described herein.

30 **HPLC** - See L.R. Snyder and J.J. Kirkland, "Introduction to Modern Liquid Chromatography", 2nd. Ed., Wiley, NY, 1979.

Apparatus

<u>Suitable HPLC System</u>	Waters Division of Millipore or equivalent.
HPLC pump with He sparge and temperature control	Waters, model 600 or equivalent
Autosampler/injector	Waters 717, or equivalent
Autosampler 48 position tray	Waters or equivalent
UV detector	Waters PDA 996 or equivalent
Fluorescence detector	Waters 740 or equivalent
Data System/Integrator	Waters 860 or equivalent
Autosampler vials and caps	4 mL capacity, Millipore #78514 and #78515.
HPLC Column, X2	Supelcosil LC18, 5 μ m, 4.6 mm x 25 cm, Supelcosil #58298
Column Inlet Filter	Rheodyne 0.5um x 3 mm Rheodyne #7335
LC eluent membrane filters	Millipore SJHV M47 10, disposable filter funnel with 0.45- μ m membrane.
Balance	Sartorius or equivalent; precision ± 0.0001 g.
Vacuum	Sample Clarification Kit with pumps and filters, Waters #WAT085113.

Reagents

C8 LAS standard material	Sodium-p-2-octylbenzene sulfonate.
C15 LAS standard material	Sodium-p-2-pentadecylbenzene sulfonate.

ProcedureA. Preparation of HPLC mobile Phase

1. Mobile phase A
 - 5 a) Weigh 11.690 g sodium chloride and transfer to a 2000 mL volumetric flask. Dissolve in 200 mL HPLC grade water.
 - b) Add 800 mL of acetonitrile and mix. Dilute to volume after solution comes to room temperature. This prepares a solution of 100 mM NaCl/40% ACN.
 - c) Filter through an LC eluent membrane filter and degas prior to use.
- 10 2. Mobile phase B - Prepare 2000 mL of 60% acetonitrile in HPLC grade water. Filter through an LC eluent membrane filter and degas prior to use.

B. C8 and C15 Internal Standard Solution

1. Weigh 0.050 g of a 2-phenyloctylbenzenesulfonate and 0.050g of 2-Phenylpentadecanesulfonate standards and quantitatively transfer to a 100 mL volumetric flask.
2. Dissolve with 30 mL ACN and dilute to volume with HPLC grade water. This prepares ca. 1500-ppm solution of the mixed standard.

5 C. Sample Solutions

1. Wash Solutions - Transfer 250 μ L of the standard solution to a 1 mL autosampler vial and add 750 μ L of the wash solution. Cap and place in the autosampler tray.
2. Alkylbenzene sulfonic acid or Alkylbenzene sulfonate - Weigh 0.10 g of the alkylbenzene sulfonic acid or salt and quantitatively transfer to a 100 mL volumetric flask. Dissolve with 30 mL ACN and dilute to volume with HPLC grade water. Transfer 250 μ L of the standard solution to a 1 mL autosampler vial and add 750 μ L of the sample solution. Cap and place in the autosampler tray. If solution is excessively turbid, filter through 0.45 μ m membrane before transferring to auto-sampler vial. Cap and place in the auto-sampler tray.

10 D. HPLC System

1. Prime HPLC pump with mobile phase. Install column and column inlet filter and equilibrate with eluent (0.3 mL/min for at least 1 hr.).
2. Run samples using the following HPLC conditions:

Mobile phase A 100 mM NaCl/40% ACN

Mobile phase B 40% H₂O/60% ACN

time 0 min. 100% Mobile phase A 0% Mobile Phase B

time 75 min. 5% Mobile phase A 95% Mobile Phase B

time 98 min. 5% Mobile phase A 95% Mobile Phase B

time 110 min. 100% Mobile phase A 0% Mobile Phase B

time 120 min. 100% Mobile phase A 0% Mobile Phase B

20 Note: A gradient delay time of 5-10 minutes may be needed depending on dead volume of HPLC system.

Flow rate 1.2 mL/min.

Temperature 25°C

He sparge rate 50 mL/hr.

UV detector 225 nm

Fluorescence detector $\lambda = 225$ nm, $\lambda = 295$ nm with sensitivity at 10 x.

Run time	120 min.
Injection volume	10 μ L
Replicate injections	2
Data rate	0.45 MB/Hr.
Resolution	4.8nm

3. The column should be washed with 100% water followed by 100% acetonitrile and stored in 80/20 ACN/water.

The HPLC elution time of the 2-phenyloctylbenzenesulfonate defines the lower limit and the elution time of the 2-phenylpentadecanesulfonate standard defines the upper limit of the

5 HPLC analysis relating to the alkylbenzene sulfonic acid/salt mixture of the invention. If 90% of the alkylbenzene sulfonic acid/salt mixture components have retention times within the range of the above standards then the sample can be further defined by methods NMR 3 and NMR 4.

If the alkylbenzene sulfonic acid/salt mixture contains 10% or more of components outside the retention limits defined by the standards then the mixture should be further purified by

10 method HPLC-P or by DE, DIS methods.

HPLC Preparative (HPLC-P) - Alkylbenzene sulfonic acids and/or the salts which contain substantial impurities (10% or greater) are purified by preparative HPLC. See L.R. Snyder and J.J. Kirkland, "Introduction to Modern Liquid Chromatography", 2nd. Ed., Wiley, NY, 1979. This is routine to one skilled in the art. A sufficient quantity should be purified to meet the requirements of the NMR 3 and NMR 4.

Preparative LC method using Mega Bond Elut Sep Pak® (HPLC-P)

Alkylbenzene sulfonic acids and/or the salts which contain substantial impurities (10% or greater) can also be purified by an LC method (also defined herein as HPLC-P). This procedure is actually preferred over HPLC column prep purification.

20 As much as 500 mg of unpurified alkylbenzene sulfonic salt can be loaded onto a 10g(60ml) Mega Bond Elut Sep Pak® and with optimized chromatography the purified salt can be isolated and ready for freeze drying within 2 hours. A 100 mg sample of alkylbenzene sulfonate salt can be loaded onto a 5g(20ml) Bond Elut Sep Pak and ready within the same amount of time.

25 A. Instrumentation

HPLC: Waters Model 600E gradient pump, Model 717 Autosampler, Water's Millennium PDA, Millennium Data Manager (v. 2.15)

Mega Bond Elut: C18 bonded phase, Varian 5g or 10g, PN:1225-6023, 1225-6031 with adaptors

HPLC Columns: Supelcosil LC-18 (X2), 250x4.6mm, 5mm; #58298

Analytical Balance: Mettler Model AE240, capable of weighing samples to ± 0.01 mg

B. Accessories

Volumetrics: glass, 10mL

5 Graduated Cylinder: 1L

HPLC Autosampler Vials: 4mL glass vials with Teflon caps and glass low volume inserts and pipette capable of accurately delivering 1, 2, and 5mL volumes

C. Reagents and Chemicals

Water (DI-H₂O): Distilled, deionized water from a Millipore, Milli-Q system or equivalent

10 Acetonitrile (CH₃CN): HPLC grade from Baker or equivalent Sodium Chloride Crystal Baker Analyzed or equivalent

D. HPLC Conditions

Aqueous Phase Preparation:

15 A: To 600mL of DI-H₂O contained in a 1L-graduated cylinder, add 5.845 of sodium chloride. Mix well and add 400 ml ACN. Mix well.

B: To 400ml of DI-H₂O contained in a 1L graduated cylinder, add 600ml ACN and mix well.

Reservoir A: 60/40, H₂O/CAN with salt and Reservoir B: 40/60, H₂O/ACN

Run Conditions: Gradient: 100% A for 75 min. 5%A/ 95% B for 98 min. 5%A/95% B for 20 110min. 100%A for 125min.

Column Temperature Not Thermostatted (i.e., room temp.)

HPLC Flow Rate 1.2mL/min

Injection Volume 10mL

Run Time 125 minutes

25 UV Detection 225nm

Conc. >4mg/ml

SEP PAK EQUILIBRATION (BOND ELUT, 5G)

1. Pass 10 ml of a solution containing 25/75 H₂O/ACN onto the sep pak by applying positive pressure with a 10 cc syringe at a rate of ~ 40 drops/min. Do not allow the sep pak to go dry.
- 30 2. Immediately pass 10ml (x3) of a solution containing 70/30 H₂O/ACN in the same manner as #1. Do not allow the sep pak to go dry. Maintain a level of solution (~1mm) at the head of the sep pak.
3. The sep pak is now ready for sample loading.

SAMPLE

LOADING/ SEPARATION AND ISOLATION

4. Weigh <200 mg of sample into a 1 dram vial and add 2 ml of 70/30 H₂O/ACN. Sonicate and mix well.
5. Load sample onto Bond Elut and with positive pressure from a 10 cc syringe begin separation. Rinse vial with 1 ml (x2) portions of the 70/30 solution and load onto sep pak. Maintain ~1mm of solution at the head of the sep pak.
6. Pass 10 ml of 70/30 onto the Bond Elut with positive pressure from a 10 cc syringe at a rate of ~40 drops/min.
7. 4. Repeat this with 3 ml and 4 ml and collect effluent if interested in impurities.

ISOLATION AND COLLECTION

- 10 1. Pass 10 ml of solution containing 25/75 H₂O/ACN with positive pressure from a 10 cc syringe and collect effluent. Repeat this with another 10 ml and again with 5 ml. The purified alkylbenzene sulfonic acid salt is now ready for freeze drying and subsequent characterization.
- 15 2. Rotovap until ACN is removed and freeze dry the remaining H₂O. Sample is now ready for chromatography.

Note: When incorporating the Mega Bond Elut Sep Pak (10 g version) up to 500 mg of sample can be loaded onto the sep pak and with solution volume adjustments, the effluent can be ready for freeze drying within 2 hours.

SEP PAK EQUILIBRATION (BOND ELUT, 10G)

- 20 1. Pass 20 ml of a solution containing 25/75 H₂O/ACN onto the sep pak using laboratory air or regulated cylinder air at a rate which will allow ~ 40 drops/min. You cannot use positive pressure from a syringe because it is not sufficient to move the solution thru the sep pak. Do not allow the sep pak to go dry.
- 25 2. Immediately pass 20ml (x2) and an additional 10 ml of a solution containing 70/30 H₂O/ACN in the same manner as #1. Do not allow the sep pak to go dry. Maintain a level of solution (~1mm)at the head of the sep pak.
- 30 3. The sep pak is now ready for sample loading.

SAMPLE LOADING/SEPARATION AND ISOLATION

1. Weigh <500 mg of sample into a 2 dram vial and add 5 ml of 70/30 H₂O/ACN. Sonicate and mix well.
- 30 2. Load sample onto Bond Elut and with positive pressure from an air source begin separation. Rinse vial with 2 ml (x2) portions of the 70/30 solution and put onto the sep pak. Maintain ~1mm of solution at the head of the sep pak.

3. Pass 20 ml of 70/30 onto the Bond Elut with positive pressure from an air source at a rate of ~40 drops/min. Repeat this with 6 ml and 8 ml and collect effluent if interested in impurities.

ISOLATION AND COLLECTION

1. Pass 20 ml of solution containing 25/75 H₂O/ACN with positive pressure from an air source and collect effluent.
2. Repeat this with another 20 ml and again with 10 ml. This isolated fraction contains the pure MLAS.
3. The isolated alkylbenzene sulfonic acid salt is now ready for freeze drying and subsequent characterization.
- 10 4. Rotovap until ACN is removed and freeze dry the remaining H₂O. Sample is now ready for chromatography.

Note: Adjustments in organic modifier concentration may be necessary for optimum separation and isolation.

DISTILLATION (DIS) - A 5-liter, 3-necked round bottom flask with 24/40 joints is equipped with a magnetic stir bar. A few boiling chips (Hengar Granules, catalog #136-C) are added to the flask. A 9 1/2-inch long vigreux condenser with a 24/40 joint is placed in the center neck of the flask. A water-cooled condenser is attached to the top of the vigreux condenser which is fitted with a calibrated thermometer. A vacuum-receiving flask is attached to the end of the condenser. A glass stopper is placed in one side arm of the 5-liter flask and a calibrated thermometer in the other. The flask and the vigreux condenser are wrapped with aluminum foil. To the 5-liter flask, is added 2270 g of an alkylbenzene mixture which contains 10% or more impurities as defined by the GC method. A vacuum line leading from a vacuum pump is attached to the receiving flask. The alkylbenzene mixture in the 5-liter flask is stirred and vacuum is applied to the system. Once the maximum vacuum is reached (at least 1 inch of Hg pressure by gauge or less), the alkylbenzene mixture is heated by means of an electric heating mantle. The distillate is collected in two fractions. Fraction A is collected from about 25°C to about 90°C as measured by the calibrated thermometer at the top of the vigreux column. Fraction B is collected from about 90°C to about 155°C as measured by the calibrated thermometer at the top of the vigreux column. Fraction A and pot residues (high boiling) are discarded. Fraction B (1881 g) contains the alkylbenzene mixture of interest. The method can be scaled according to the practitioner's needs provided that sufficient quantity of the alkylbenzene mixture remains after distillation for evaluation by NMR methods NMR1 and NMR2.

ACIDIFICATION (AC) - Salts of alkylbenzene sulfonic acids are acidified by common means such as reaction in a solvent with HCl or sulfuric acid or by use of an acidic resin such as

Amberlyst 15. Acidification is routine to one skilled in the art. After acidifying remove all solvents, especially any moisture, so that the samples are anhydrous and solvent-free.

Note: For all of the below NMR test methods, the chemical shifts of the NMR spectrum are either externally or internally referenced to TMS in CDCl_3 , i.e. chloroform.

5 **NMR 1**

^{13}C -NMR 2/3-Phenyl Index for Alkylbenzene Mixtures

A 400 mg sample of an alkylbenzene mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a standard NMR tube. The ^{13}C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 10 40° ^{13}C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The region of the ^{13}C NMR spectrum between about 145.00 ppm to about 150.00 ppm is integrated. The 2/3-Phenyl index of an alkylbenzene mixture is defined by the following equation:

2/3-Phenyl Index = (Integral from about 147.65 ppm to about 148.05 ppm)/(Integral from about 145.70 ppm to about 146.15 ppm) x 100

15 **NMR 2**

^{13}C -NMR 2-Methyl-2-Phenyl Index

A 400 mg sample of an anhydrous alkylbenzene mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a standard NMR tube. The ^{13}C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 40° ^{13}C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The ^{13}C NMR spectrum region between about 145.00 ppm to about 150.00 ppm is integrated. The 2-methyl-2-phenyl index of an alkylbenzene mixture is defined by the following equation:

2-methyl-2-phenyl index = (Integral from about 149.35 ppm to about 149.80 ppm)/(Integral from about 145.00 ppm to about 150.00 ppm).

25 **NMR 3**

^{13}C -NMR 2/3-Phenyl Index for Alkylbenzene sulfonic Acid Mixtures

A 400 mg sample of an anhydrous alkylbenzene sulfonic acid mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a standard NMR tube. The ^{13}C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 40° ^{13}C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The ^{13}C NMR spectrum region between about 152.50 ppm to about 156.90 ppm is integrated. The 2/3-Phenyl Index of an alkylbenzene sulfonic acid mixtures defined by the following equation:

2/3-Phenyl Index = (Integral from about 154.40 to about 154.80 ppm)/(Integral from about 152.70 ppm to about 153.15 ppm) x 100

NMR 4

¹³C-NMR 2-Methyl-2-Phenyl Index for Alkylbenzene sulfonic Acid Mixtures

5 A 400 mg sample of an anhydrous alkylbenzene sulfonic acid mixture is dissolved in 1 ml of anhydrous deuterated chloroform containing 1% v/v TMS as reference and placed in a standard NMR tube. The ¹³C NMR is run on the sample on a 300 MHz NMR spectrometer using a 20 second recycle time, a 40° ¹³C pulse width and gated heteronuclear decoupling. At least 2000 scans are recorded. The ¹³C NMR spectrum region between about 152.50 ppm to about 156.90 ppm is integrated. The 2-methyl-2-phenyl Index for an alkylbenzene sulfonic acid mixture is defined by the following equation:

10 2-methyl-2-phenyl index = (Integral from about 156.40 ppm to about 156.65 ppm)/(Integral from about 152.50 ppm to about 156.90 ppm).

Detergent Composition Examples

15 Typical ingredients often referred to as "minors" can include perfumes, dyes, pH agents.

The following example is illustrative of the present invention, but is not meant to limit or otherwise define its scope. All parts, percentages and ratios used are expressed as percent weight unless otherwise noted.

EXAMPLE 1

20 The following laundry detergent compositions A to F are prepared in accordance with the invention:

	A	B	C	D	E	F
MLAS	22	16.5	11	1 - 5.5	10 - 25	5-35
Any Combination of: C45AS C45E1S or C23E3S LAS C26 SAS C47 NaPS C48 MES MBA16.5S MBA15.5E2S	0	1 - 5.5	11	16.5	0 - 5	0-10
QAS	0 - 2	0 - 2	0 - 2	0 - 2	0 - 4	0
C23E6.5 or C45E7	1.5	1.5	1.5	1.5	0 - 4	0 - 4
Zeolite A	27.8	0	27.8	27.8	20 - 30	0
Zeolite MAP	0	27.8	0	0	0	0
STPP	0	0	0	0	0	5-65
PAA	2.3	2.3	2.3	2.3	0 - 5	0 - 5
Carbonate	27.3	27.3	27.3	27.3	20 - 30	0 - 30

Silicate	0.6	0.6	0.6	0.6	0 - 2	0 - 6
PB1	1.0	1.0	0-10	0-10	0 - 10	0 - 20
NOBS	0-1	0-1	0-1	0.1	0.5-3	0 - 5
LOBS	0	0	0-3	0	0	0
TAED	0	0	0	2	0	0 - 5
MnCAT	0	0	0	0	2ppm	0 - 1
Protease	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 1
Cellulase	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.5	0 - 1
Amylase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 1	0 - 1
SRP 1 or SRP 2	0.4	0.4	0.4	0.4	0 - 1	0 - 5
Brightener 1 or 2	0.2	0.2	0.2	0.2	0 - 0.3	0 - 5
PEG	1.6	1.6	1.6	1.6	0 - 2	0 - 3
Silicone Antifoam	0.42	0.42	0.42	0.42	0 - 0.5	0 - 1
Sulfate, Water, Minors	to 100%	to 100%				
Density (g/L)	400-700	600-700	600-700	600-700	600 - 700	450-750

EXAMPLE 2

The following laundry detergent compositions G to J suitable for hand-washing soiled fabrics are prepared in accord with the invention:

	G	H	I	J
MLAS	18	22	18	22
STPP	20	40	22	28
Carbonate	15	8	20	15
Silicates	15	10	15	10
Protease	0	0	0.3	0.3
Perborate	0	0	0	10
Sodium Chloride	25	15	20	10
Brightener	0 - 0.3	0.2	0.2	0.2
Moisture & Minors	---Balance---			

5

EXAMPLE 3

Cleaning Product Compositions

The following liquid laundry detergent compositions K to O are prepared in accord with the invention. Abbreviations are as used in the preceding Examples.

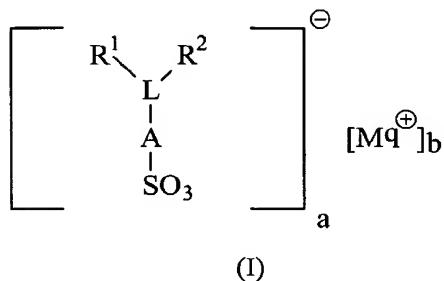
10

	K	L	M	N	O
MLAS	1 - 7	7 - 12	12 - 17	17 - 22	1 - 35

Any combination of: C25E1.8-2.5S MBA15.5E1.8S MBA15.5S C25AS (linear to high 2-alkyl) C47 NaPS C26 SAS LAS C26 MES	15 - 21	10 - 15	5 - 10	0 - 5	0 - 25
LMFAA	0 - 3.5	0 - 3.5	0 - 3.5	0 - 3.5	0 - 8
C23E9 or C23E6.5	0 - 2	0 - 2	0 - 2	0 - 2	0 - 8
APA	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 2
Citric Acid	5	5	5	5	0 - 8
Fatty Acid (TPK or C12/14)	2	2	2	2	0 - 14
EtOH	4	4	4	4	0 - 8
PG	6	6	6	6	0 - 10
MEA	1	1	1	1	0 - 3
NaOH	3	3	3	3	0 - 7
Hydrotrope or NaTS	2.3	2.3	2.3	2.3	0 - 4
Formate	0.1	0.1	0.1	0.1	0 - 1
Borax	2.5	2.5	2.5	2.5	0 - 5
Protease	0.9	0.9	0.9	0.9	0 - 1.3
Lipase	0.06	0.06	0.06	0.06	0 - 0.3
Amylase	0.15	0.15	0.15	0.15	0 - 0.4
Cellulase	0.05	0.05	0.05	0.05	0 - 0.2
PAE	0 - 0.6	0 - 0.6	0 - 0.6	0 - 0.6	0 - 2.5
PIE	1.2	1.2	1.2	1.2	0 - 2.5
PAEC	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 2
SRP 2	0.2	0.2	0.2	0.2	0 - 0.5
Brightener 1 or 2	0.15	0.15	0.15	0.15	0 - 0.5
Silicone antifoam	0.12	0.12	0.12	0.12	0 - 0.3
Fumed Silica	0.0015	0.0015	0.0015	0.0015	0-0.003
Perfume	0.3	0.3	0.3	0.3	0 - 0.6
Dye	0.0013	0.0013	0.0013	0.0013	0-0.003
Moisture/minors	Balance	Balance	Balance	Balance	Balance
Product pH (10% in DI water)	7.7	7.7	7.7	7.7	6 - 9.5

What is claimed is:

1. An enhanced alkylbenzene sulfonate surfactant mixture comprising:
 - (a) from about 60% to about 25% by weight of a mixture of enhanced alkylbenzene sulfonates having formula (I):

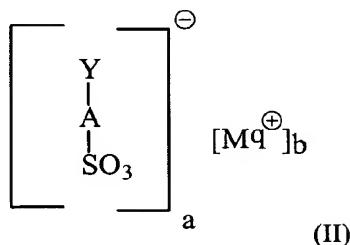


(I)

wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen, said L having two methyl termini and said L having no substituents other than A, R¹ and R²; and wherein said mixture of enhanced alkylbenzene sulfonates contains two or more of said enhanced alkylbenzene sulfonates differing in molecular weight of the anion of said formula (I) and wherein said mixture of enhanced alkylbenzene sulfonates has

- a sum of carbon atoms in R¹, L and R² of from 9 to 15;
- an average aliphatic carbon content of from about 10.0 to about 14.0 carbon atoms; M is a cation or cation mixture having a valence q; a and b are integers selected such that said enhanced alkylbenzene sulfonates are electroneutral; R¹ is C₁-C₃ alkyl; R² is selected from H and C₁-C₃ alkyl; A is a benzene moiety; and

(b) from about 40% to about 75% by weight of a mixture of modified unsubstituted alkylbenzene sulfonates having formula (II):



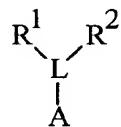
(II)

wherein a, b, M, A and q are as defined hereinbefore and Y is an unsubstituted linear aliphatic moiety consisting of carbon and hydrogen having two methyl termini, and wherein said Y has a sum of carbon atoms of from 9 to 15, preferably from 10 to 14, and said Y has an average aliphatic carbon content of from about 10.0 to about 14.0; and

wherein said enhanced alkylbenzene sulfonate surfactant mixture is further characterized by a 2/3-phenyl index of from about 275 to about 10,000.

2. An enhanced alkylbenzene mixture comprising:

(a) from about 60% to about 25% by weight of a mixture of enhanced alkylbenzenes having formula (I):



(I)

wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen, said L having two methyl termini and said L having no substituents other than A, R1 and R2; and wherein said mixture of enhanced alkylbenzenes contains two or more of said enhanced alkylbenzenes differing in molecular weight of said formula (I) and wherein said mixture of enhanced alkylbenzenes has

- a sum of carbon atoms in R1, L and R2 of from 9 to 15;
- an average aliphatic carbon content of from about 10.0 to about 14.0 carbon atoms; R1 is C1-C3 alkyl; R2 is selected from H and C1-C3 alkyl; A is a benzene moiety; and

(b) from about 40% to about 75% by weight of a mixture of modified unsubstituted alkylbenzenes having formula (II):



(II)

wherein A is as defined hereinbefore and Y is an unsubstituted linear aliphatic moiety consisting of carbon and hydrogen having two methyl termini, and wherein said Y has a sum of carbon atoms of from 9 to 15, preferably from 10 to 14, and said Y has an average aliphatic carbon content of from about 10.0 to about 14.0; and

wherein said enhanced alkylbenzene mixture is further characterized by a 2/3-phenyl index of from about 275 to about 10,000.

3. An enhanced alkylbenzene sulfonate surfactant mixture according to Claim 1 wherein M is selected from H, Na, K and mixtures thereof; a=1; b=1; q=1; and said enhanced alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than about 0.3; preferably

wherein the mixture is the product of a process using as catalyst a zeolite selected from mordenite, offretite and H-ZSM-12 in at least partially acidic form; preferably wherein the mixture is the product of a process using as a catalyst any catalyst that exhibits the same or similar characteristics as said mordenite, under the same or similar conditions of said process.

4. A detergent composition comprising:

- a) from about 0.1% to about 95%, by weight of enhanced alkylbenzene sulfonate surfactant mixture according to Claim 3;
- b) from about 0.00001% to about 99.9%, by weight of conventional cleaning adjuncts other than surfactants; and
- c) from 0% to about 50%, by weight, of a surfactant other than said enhanced alkylbenzene sulfonate surfactant mixture;

provided that when said detergent composition comprises any other alkylbenzene sulfonate than the alkylbenzene sulfonate of said enhanced alkylbenzene sulfonate surfactant mixture, said enhanced alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate, as a mixture, have an overall 2/3-phenyl index of from about 275 to about 10,000.

5. A medium 2/3-phenyl surfactant mixture consisting essentially of:

- a) from 1% to about 60% by weight of a first alkylbenzene sulfonate surfactant, wherein said first alkylbenzene sulfonate surfactant is a enhanced alkylbenzene sulfonate surfactant mixture according to Claim 1; and
- b) from 40% to about 99%, by weight of a second alkylbenzene sulfonate surfactant, wherein said second alkylbenzene sulfonate surfactant is an alkylbenzene sulfonate surfactant mixture other than said enhanced alkylbenzene sulfonate surfactant mixture according to Claim 1, and wherein said second alkylbenzene sulfonate surfactant has a 2/3-phenyl index of from about 75 to about 160;

provided that said medium 2/3-phenyl surfactant mixture has a 2/3-phenyl index of from about 160 to about 275.

6. A detergent composition comprising:

- (a) from about 0.1% to about 95% by weight of medium 2/3-phenyl surfactant mixture according to Claim 5;
- (b) from about 0.00001% to about 99.9% by weight of conventional cleaning adjuncts other than surfactants; and

(c) from 0% to about 50% by weight of a surfactant other than said medium 2/3-phenyl surfactant mixture;

provided that when said detergent composition comprises any other alkylbenzene sulfonate than the alkylbenzene sulfonate of said medium 2/3-phenyl surfactant mixture, said medium 2/3-phenyl surfactant mixture and said other alkylbenzene sulfonate, as a mixture, have an overall 2/3-phenyl index of from about 160 to about 275.

7. A process for preparing a medium 2/3-phenyl surfactant mixture according to Claim 5 comprising a step selected from:

- (i) blending said first alkylbenzene sulfonate surfactant and said second alkylbenzene sulfonate surfactant; and
- (ii) blending the nonsulfonated precursor of said first alkylbenzene sulfonate surfactant and the nonsulfonated precursor of said second alkylbenzene sulfonate surfactant and sulfonating said blend.

8. A detergent composition comprising:

- (a) from about 1% to about 50%, by weight of the product of the process of Claim 7; and
- (b) from about 0.00001% to about 99.9%, by weight of conventional cleaning adjuncts other than surfactants.

9. A detergent composition according to Claim 6 or 8 wherein said conventional cleaning adjunct other than surfactants is selected from the group consisting of builders, detersive enzymes, bleaching systems, brighteners, at least partially water-soluble or water dispersible polymers, abrasives, bactericides, tarnish inhibitors, dyes, solvents, hydrotropes, perfumes, thickeners, antioxidants, processing aids, suds boosters, suds suppressors, buffers, anti-fungal agents, mildew control agents, insect repellents, anti-corrosive aids, chelants and mixtures thereof.

10. A method comprising treating a fabric with the detergent composition of Claim 6 or 8.

11. An enhanced alkylbenzene sulfonate surfactant mixture comprising the product of a process comprising the steps of:

- (I) alkylating benzene with an alkylating mixture;
- (II) sulfonating the product of (I); and
- (III) neutralizing the product of (II);

wherein said alkylating mixture comprises:

- (a) from about 1% to about 99.9%, by weight of methyl-substituted C₉-C₂₀ monoolefins, said methyl-substituted monoolefins having structures identical with those of the branched monoolefins formed by dehydrogenating branched paraffins of formula R¹LR² wherein L is an acyclic aliphatic moiety consisting of carbon and hydrogen and containing two terminal methyls; R¹ is C₁ to C₃ alkyl; and R² is selected from H and C₁ to C₃ alkyl; and
- (b) from about 0.1% to about 85%, by weight of C₉-C₂₀ linear aliphatic olefins; preferably wherein said alkylating mixture contains said branched C₉-C₂₀ monoolefins having at least two different carbon numbers in said C₉-C₂₀ range, and has a mean carbon content of from about 9.0 to about 15.0 carbon atoms; and wherein said components (a) and (b) are at a weight ratio of at least about 15:85.

12. A detergent composition comprising:

- (a) from about 1% to about 50%, by weight of enhanced alkylbenzene sulfonate surfactant mixture according to Claim 1, wherein said enhanced alkylbenzene sulfonate surfactant mixture has a 2-methyl-2-phenyl index of less than about 0.3;
- (b) from about 0.000001% to about 10%, by weight of a member selected from the group consisting of optical brighteners, dyes, photobleaches, hydrophobic bleach activators and transition metal bleach catalysts;
- (c) from 0.1% to about 40% by weight of surfactants selected from the group consisting of cationic surfactants, nonionic surfactants, anionic surfactants, and amine oxide surfactants; and
- (d) from about 10% to about 99%, by weight of conventional cleaning adjuncts; provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said enhanced alkylbenzene sulfonate surfactant mixture, said detergent composition is further characterized by an overall 2/3-phenyl index of at least about 200, wherein said overall 2/3-phenyl index is determined by measuring 2/3-phenyl index, as defined herein, on a blend of said enhanced alkylbenzene sulfonate surfactant mixture and said any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of said enhanced alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition; and

further provided that when said detergent composition comprises any alkylbenzene sulfonate surfactant other than said enhanced alkylbenzene sulfonate surfactant mixture, said detergent composition is further characterized by an overall 2-methyl-2-phenyl index of less than about 0.3, wherein said overall 2-methyl-2-phenyl index is to be determined by measuring 2-methyl-2-phenyl index, as defined herein, on a blend of said enhanced alkylbenzene sulfonate surfactant mixture and any other alkylbenzene sulfonate to be added to said detergent composition, said blend, for purposes of measurement, being prepared from aliquots of said enhanced alkylbenzene sulfonate surfactant mixture and said other alkylbenzene sulfonate not yet exposed to any other of said components of the detergent composition.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/15480

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 43473 A (PROCTER & GAMBLE) 27 July 2000 (2000-07-27) page 36 -page 48; examples 1-24 page 80, paragraphs 3,4 claims 1-8 ---	1-12
X	WO 00 23549 A (PROCTER & GAMBLE) 27 April 2000 (2000-04-27) page 42 -page 54; examples 1-24 page 109, line 30 -page 110, line 7 claims 1-16 ---	1-12
X	WO 00 23548 A (PROCTER & GAMBLE) 27 April 2000 (2000-04-27) page 93, line 19-31 claims 1-9 ---	1,3-12
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

^a Special categories of cited documents :

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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

6 August 2002

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/15480

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 05242 A (PROCTER & GAMBLE) 4 February 1999 (1999-02-04) page 4, last paragraph -page 6, paragraph 3 page 15 -page 16; example 5 page 68; example 12 -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 02/15480

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